

Research Progress of N-type MgSb based Thermoelectric Materials

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Abstract

N-type Mg_3Sb_2 -based thermoelectric materials have garnered significant attention due to their excellent thermoelectric performance in the low to medium temperature range (300 – 700 K), abundant elemental reserves, and low cost. This paper systematically reviews recent research progress in n-type Mg_3Sb_2 -based thermoelectric materials, with a focus on preparation methods, performance enhancement strategies, and application prospects. Key synthesis techniques, including solid-state reaction, mechanical alloying combined with spark plasma sintering (SPS), rapid solidification, and flux/molten salt growth, are discussed in detail, highlighting their respective process characteristics, microstructural control mechanisms, and influences on thermoelectric properties. To improve the thermoelectric figure of merit (ZT), strategies such as carrier and band engineering, multiscale phonon scattering, and defect regulation are emphasized. These approaches aim to decouple electron and phonon transport, thereby enhancing the power factor while reducing lattice thermal conductivity. Furthermore, this review explores the potential applications of n-type Mg_3Sb_2 -based materials in waste heat recovery and solid-state cooling, addressing key challenges related to module integration, interfacial stability, and scalability. Finally, future research directions and practical implementation pathways are proposed to facilitate the development and deployment of high-performance Mg-Sb thermoelectric systems.

Keywords

Thermoelectric Materials; N-type Mg_3Sb_2 ; Preparation Methods; Band Engineering; Lattice Thermal Conductivity; Carrier Transport; Waste Heat Recovery; Spark Plasma Sintering.

1. Research Background and Meaning

In today's world, the shortage of fossil fuels and environmental pollution have become increasingly prominent issues. The diversification and efficient utilization of energy have emerged as a crucial approach to systematically address these challenges. Statistics show that over 60% of energy consumed in industrial activities is dissipated into the atmosphere as waste heat. Therefore, developing clean energy and improving energy efficiency have become top priorities for sustainable development in human society.

Among various new energy material systems, thermoelectric materials stand out for their unique advantages. By harnessing microscopic charge carrier motion within the material, they enable direct conversion between thermal and electrical energy, making them crucial for applications like thermoelectric power generation and solid-state refrigeration [1-5]. Since the discovery of the thermoelectric effect in the 1920s, these materials have garnered widespread attention. Significant progress has been made in thermoelectric science and technology, particularly through deepened

understanding of transport mechanisms in thermoelectric semiconductors, rapid advancements in multi-scale structural control and fabrication techniques, and the development of novel design theories. These advancements have not only driven the creation of high-performance thermoelectric materials but also expanded the scope of thermoelectric material science and energy conversion technologies [6-9]. Devices based on thermoelectric materials boast advantages such as compact size, rapid response, absence of mechanical moving parts, environmental friendliness, and easy maintenance, which have led to their widespread adoption. In aerospace engineering, thermoelectric power generation technology utilizes heat from radioactive isotope decay to power space probes conducting scientific missions in outer space. For civilian applications, generating electricity from industrial waste heat and automotive exhaust residual heat has gained significant attention. Major automakers including General Motors and Toyota have conducted applied research on integrating thermoelectric power modules with vehicle systems. In solid-state cooling applications, thermoelectric cooling devices can provide localized thermal management for precision instruments such as medical equipment, high-performance receivers, electronic chips, and integrated circuits.

It is widely recognized that conventional heat engines achieve a power generation efficiency of 35%. In contrast, even the currently commercial Bi₂Te₃-based thermoelectric materials demonstrate only about 6% conversion efficiency, significantly lower than conventional heat engines' efficiency. This substantial gap has substantially hindered their practical implementation. The primary constraints on thermoelectric device efficiency stem from multiple factors: high material costs, limited intrinsic properties, thermal degradation at elevated temperatures, and high interfacial contact resistance. Therefore, developing cost-effective, high-performance thermoelectric materials with stable properties, along with designing innovative high-efficiency thermoelectric devices, holds crucial practical significance for advancing large-scale applications of thermoelectric energy conversion technology.

In recent years, the emerging n-type Mg₃Sb₂-based thermoelectric materials have demonstrated excellent thermoelectric performance in low to medium temperature ranges, with ZT values comparable to Bi₂Te₃-based materials, attracting widespread attention. Moreover, magnesium's abundant content and cost-effectiveness (4.6 USD/kg), approximately one-tenth that of tellurium, significantly reduces material costs, showcasing promising application potential. However, due to the relatively recent attention given to n-type Mg₃Sb₂-based thermoelectric materials, their microstructural characteristics and carrier transport mechanisms remain incompletely elucidated, while material performance still requires further improvement, limiting practical implementation. This paper reviews the research progress in n-type Mg₃Sb₂-based thermoelectric materials.

2. Preparation Method and Characteristics of MgSb based Thermoelectric Materials

2.1 Solid Phase Reaction/Solid State Synthesis

2.1.1 Process Flow

(1) Raw materials and ratios

Raw materials: Mg pellet/ingot ($\geq 99.9\%$), Sb powder ($\geq 99.999\%$), a small amount of pre-hydrogenated binary compound can be used as precursor when necessary.

Ratio: weigh according to the target Mg_3Sb_2 stoichiometry (e.g., MgSb), and excess Mg 5-10 at.% to compensate for volatilization. The scale accuracy is recommended to be less than or equal to 10 g.

Pre-treatment: Sb powder is dried in vacuum for 2 hours at 120 °C to remove moisture; graphite paper, mold and other consumables are dried/vacuumed before use.

(2) Inert protection and mixing

Environment: Operate Mg_3Sb_2 in an Ar glove box (O/H₂O < 0.1 ppm).

Pre-mixing: the agate Mg_3Sb_2 or ZrO₂ medium is ground for 20-30 min (or hand grinding) to improve uniformity and avoid premature reaction and contamination caused by high energy.

(3) Sealing and encapsulation

Container: BN crucible lining → Ta tube sealing (argon arc welding) → double layer packaging of quartz casing.

Protection: After pumping 10^{-3} to 5×10^{-5} Pa, seal it, or fill with 0.2 atm high purity Ar and then seal it to reduce the risk of Mg vapor escape.

(4) Programmed thermal solid-state reaction

200-250 °C/2 h degassing → 450-500 °C/6-10 h pre-reaction (to avoid sudden and violent reaction of Mg) → 650-700 °C/10-20 h main reaction.

Cooling: furnace cooling or 2-5 °C·min controlled cooling to reduce thermal stress and phase separation risk.

(5) Crushing and high energy grinding (mechanical activation)

Objective: Refine the grain size and homogeneity to prepare the particle size distribution for SPS densification.

Typical parameters: speed 300-500 rpm, ball ratio 10:1-15:1, total time 2-6 h (intermittent with temperature control), 0.2-0.5 wt% paraffin/graphite can be added for granulation and antioxidant additives if necessary.

(6) Forming and SPS densification

Mold: graphite mold + graphite paper lining, vacuum or Ar protection.

Typical parameters: 600-700 °C (873-973 K), 40-60 MPa, 5-10 min, heating 50-100 °C·min.⁻¹

Objective: relative density $\geq 95\%$, clean interface, low porosity, and controllable second phase.

(7) Post-processing and characterization

Annealing: 450-550 °C/4-12 h to eliminate residual stress, promote defect rearrangement and homogenization.

Characterization: XRD/Rietveld phase identification and quantification, density (Archimedes method), oxygen content (LECO), SEM/EDS microzone composition, Hall and Pisarenko analysis carrier concentration-effective mass coupling.

2.1.2 Key Process Control Points

Mg volatilization: magnesium excess, double layer packaging, shorten the high temperature insulation time and use segmented heating to inhibit weight loss.

Oxygen pollution/clogging: inert protection in the whole process; powder, mold, graphite paper and quartz tube need to be pre-dried and vacuum.

Secondary phase/unevenness: prolong the low temperature pre-reaction to promote complete reaction; high energy ball milling before SPS improves solid solution and particle size distribution; subsequent annealing promotes homogenization.

Porosity and density: Optimize SPS pressure/temperature/insulation time and powder D (recommended 5-20 μm) to avoid excessive grain coarsening.

Interface barrier: annealing promotes low energy interface rearrangement and maintains interface cleanliness to protect electron mobility.

2.1.3 Methodological Features

Simple process and universal equipment: conventional tubular furnace + SPS can be completed, which is convenient for amplification and batch production;

Cost-effective and highly replicable: universal raw materials, clear path, easy to establish statistical process control;

Structure-high performance flexibility: through the coordination of Mg excess, double layer packaging, program heating, ball milling activation and SPS parameters, the engineering tradeoff between charge carrier and lattice thermal conductivity can be realized;

Key Challenges and Solutions: Magnesium's high vapor pressure and reactivity require overcompensation with encapsulation and atmosphere optimization; oxygen sensitivity necessitates full-chain inert protection; secondary phases and pores require thermal insulation, cooling curve optimization, and SPS window tuning. Methodological Transfer: The combination of solid-state reaction and mechanical activation significantly reduces reaction temperature and duration while improving phase formation kinetics and grain uniformity. This approach has been validated across multiple systems and is suitable for efficient preparation of Mg-Sb brittle compound precursors and bulk materials (consistent with the original manuscript's reference methodology). Key Challenges and Solutions: Magnesium's high vapor pressure and reactivity require overcompensation with encapsulation and atmosphere optimization; oxygen sensitivity necessitates full-chain inert protection; secondary phases and pores demand thermal insulation optimization for cooling curves and SPS window calibration. Methodological Transfer: The combination of solid-state reaction and mechanical activation significantly reduces reaction temperature and duration while improving phase formation kinetics and grain uniformity. This approach has been validated across multiple systems and is suitable for efficient preparation of Mg-Sb brittle compound precursors and bulk materials (consistent with the original manuscript's reference methodology).

2.2 Mechanical Alloying + SPS Densification

The process objective is to obtain Mg-Sb precursor powder with nanoscale/sub-micron particle size, high defect density, and highly uniform composition through high-energy ball milling-induced solid-state reaction/amorphogenesis and supersaturated β_2 solid solution formation at room temperature or medium-low temperatures. Subsequently, rapid short-term SPS densification is applied to achieve both high relative density and phonon-advantaged hierarchical scattering structures, thereby establishing a foundation for optimizing electrical transport in n-type Mg-Sb materials (e.g., MgSb-based).

2.2.1 Process Flow

(1) Raw materials and ratios

Raw materials: Mg particle/rod ($\geq 99.9\%$), Sb powder ($\geq 99.999\%$); trace doping can be introduced as needed (such as Te/Se/Bi, etc.).

Ratio: measured according to the target stoichiometry, and Mg is overfilled by 5-10 at.% to compensate for subsequent volatilization and surface oxidation losses.

Pre-treatment: All powder/mold/graphite paper was pre-dried at 100-150 °C for 2 hours; the whole process was operated in an Ar glove box ($O_2, H_2O < 0.1$ ppm).

(2) Container and medium selection (pollution and wear trade-off)

Ball mill/cylinder/medium should be ZrO₂ or SiN₄; avoid stainless steel (Fe/Cr pollution) and WC (W/C introduction).

A small amount of PCA (process control agent) (e.g., stearic acid/wax) can be added to 0.2-0.5 wt% to inhibit agglomeration and cold welding; note that it should be removed later.

(3) High energy ball milling (mechanical alloying)

Equipment: planetary or SPEX swing high energy ball mill.

Typical parameters window: rotation speed 350-550 rpm; ball to material ratio 10:1-20:1; loading coefficient 1/3-1/2 tank volume; total time 5-20 h (intermittent: 30 min ball mill / 10 min stop for cooling), the outer wall temperature of the tank should be as < 60 °C as possible.

Process monitoring: XRD was taken every 2-3 h (to observe the evolution from mixture to extended peak/amorphous to nanocrystals/saturated solid solution).

(4) Dissolution, agglomeration and screening/Pre-annealing (optional)

The coarse powder was crushed and deagglomerated, and then passed through a 200-300 mesh sieve to obtain a uniform particle size distribution.

If PCA is added, it is recommended to pre-anneal at 350-450 °C for 1-2 h in an inert atmosphere to remove organic residues and stress; this step also facilitates the controlled nucleation from amorphous to nanocrystalline.

(5) Forming and SPS densification

Mold: graphite mold + graphite paper lining; vacuum (≤ 10 Pa) or Ar protection.

Typical SPS parameters: heating 50-100 °C·min⁻¹, temperature 580-680 °C, pressure 40-60 MPa, insulation 3-8 min.

Objective: The relative density should be $\geq 95-98\%$ to maintain nanoscale/submicron grains and avoid continuous second phase. In order to suppress Mg loss, pressure can be applied in the early stage of heating, the peak temperature should be focused on the lower limit and the holding time should be shortened.

(6) Subsequent annealing and characterization

Annealing: 450-550 °C / 4-12 h (Ar/vacuum) to promote phase homogenization, defect rearrangement and interface purification, while inhibiting abnormal grain growth.

Characterization: XRD/Rietveld quantitative phase analysis; SEM/TEM + EDS/EPMA observation of nano-extrusions and grain boundary networks; density (Archimedes method); O/N (LECO); Hall, Seebeck, ρ , κ , T .

2.2.2 Mechanism Characteristics and Microstructural Evolution (for Mg-Sb System)

Non-equilibrium solid solution formation and amorphous transformation: High-energy impact induces high-density accumulation of dislocations, stacking faults, and nanocrystalline boundaries, which reduces diffusion barriers and promotes short-range ordering and supersaturated solid solution formation between Mg and Sb. Partial systems transition into an amorphous state, providing energy storage conditions for subsequent "instantaneous crystallization + rapid densification" in SPS processes.

Dispersive Emission and Hierarchical Scattering: During the SPS heating and holding process, nanoscale precipitates (such as Mg-rich or Sb-rich dispersion particles) combined with submicron grain boundaries/subgrains form a multi-scale phonon scattering network, which reduces thermal conductivity. Meanwhile, back annealing is employed to adjust defect states and interfacial barriers, thereby lowering overall thermal conductivity without significantly compromising mobility.

Pulse current/contact resistance heating effect: The pulse current of SPS and particle contact resistance lead to rapid heating and surface purification of the local "neck", which is conducive to neck length and pore closure, and inhibits the adverse effects of oxide film on densification.

2.2.3 Key Parameters and Process Control Points (Practical Points)

Magnesium loss and oxygen content:

Comprehensive control by excessive Mg 5-10 at.%, shortening high temperature insulation, reducing peak temperature and double layer packaging (Ta/ quartz);

The whole process of ball grinding is loaded and unloaded in the Ar glove box to shorten the exposure time; the recommended O content of powder is $< 0.2-0.5$ wt%.

Medium contamination: priority ZrO/SiN; if WC/stainless steel is used, ICP/EDS monitoring should be done and the possible W/Fe doping effect should be explained in the discussion.

Synergy of crystal grains, pores and second phase:

The duration of ball milling should be controlled in the "sufficient reaction/overly pulverized" window (5-20 h);

SPS adopts the strategy of "low temperature + short insulation + medium and high pressure" to protect the nanostructure and suppress the pore;

The annealing temperature should not be too high (generally ≤ 550 °C) to prevent the second phase coarsening and grain boundary migration resulting in reduction.

PCA residue: pre-annealing is removed to prevent accidental phase or interface contamination induced by carbon sources.

2.2.4 Methodological Features

Low temperature/short time phase formation and high uniformity: The non-equilibrium solid solution and nanocrystalline structure induced by MA enable the subsequent SPS to achieve high density and uniform phase within a few minutes at 580-680 °C.

Strong structure-performance programmability: Through the combined regulation of ball milling duration/medium/rotation speed, PCA, SPS $\kappa_L\mu$ temperature and pressure time course, and back annealing, hierarchical phonon scattering and defect states can be controlled, taking into account both suppression and preservation.

Doped/alloy-friendly: Provides pathways for rapid and uniform incorporation of elements like Te, Se, and Bi at the solid solution and diffusion levels, reducing risks of Mg volatilization and grain coarsening caused by prolonged high-temperature treatments. Scaling potential and challenges: The equipment is versatile (high-energy ball milling + SPS), suitable for batch processing. However, it has a narrow tolerance window for medium wear/oxidation contamination and requires stringent process monitoring with comprehensive O/metal impurity detection and statistical process control (SPC). Doped/alloy-friendly: Provides pathways for rapid and uniform incorporation of elements like Te, Se, and Bi at the solid solution and diffusion levels, reducing risks of Mg volatilization and grain coarsening caused by prolonged high-temperature treatments. Scaling potential and challenges: The equipment is versatile (high-energy ball milling + SPS), suitable for batch processing; however, it has a narrow tolerance window for medium wear/oxidation contamination and requires stringent process monitoring. This necessitates comprehensive O/metal impurity monitoring and statistical process control (SPC).

2.3 Rapid Solidification (Rapid Melt Quenching/Sprue Banding) + Annealing + SPS

The process objective is to utilize high cooling rates to suppress dendrite segregation and coarse grain formation, thereby obtaining a ribbon-like precursor of fine equiaxed crystals/amorphous or supersaturated solid κ_L solutions. Controlled annealing induces dispersion precipitation and grain boundary purification (by constructing hierarchical phonon scattering networks), ultimately achieving high densification and low material properties through short-term SPS.

2.3.1 Process Flow (Recommended Steps and Parameter Window)

(1) Alloy smelting and charging

Raw materials: Mg ($\geq 99.9\%$), Sb ($\geq 99.999\%$), trace doping (Te/Se/Bi, etc.) when necessary.

Ratio: measured according to the stoichiometry, Mg is overfilled by 5-10 at.% to compensate for subsequent volatilization.

Melting environment: vacuum 10^{-3} Pa ($\leq 5 \times 10^{-2}$ Pa) after evacuation and filled with Ar (O, HO < 10 ppm). It is recommended to heat in a spray band crucible with BN lining in quartz crucible; the melt is overheated by 50-150 °C (relative to the liquid phase line).

(2) Rapid quenching of molten metal / Sprue (single roll copper wheel)

Surface line speed: 20-40 m·s⁻¹ (corresponding to cooling rate $\sim 10^5$ - 10^6 K·s⁻¹ order of magnitude).

Spray pressure: 10-50 kPa (inert gas applies pressure to the melt chamber to stabilize the jet).

Nozzle-wheel surface clearance: 0.3-0.8 mm; nozzle diameter 0.5-1.0 mm.

Band thickness/width: typical 20-60 μm / 1-3 cm; target is thin and continuous, smooth surface, no obvious perforations and oxidation stains.

Atmosphere: high purity Ar; feeding, spraying and collecting should be completed in a glove box or closed chamber as far as possible to shorten the exposure time.

Online monitoring: observe the surface finish and kink of the tape; take samples regularly for XRD (to identify amorphous peaks/expansive peaks and nanocrystalline characteristics).

(3) Strip processing and grading

Mechanical shear/light crushing to obtain about 100-500 μm flake powder;

Low temperature pre-drying (120 $^{\circ}\text{C}$ / 2 h, Ar) was used to remove moisture; strong grinding was avoided as far as possible to break the surface oxide layer and introduce contamination.

(4) Controlled annealing (structure "phase-precipitation-purification")

Objective: From amorphous/saturated solid solution to uniform nanocrystal + dispersion precipitation, release internal stress and purify grain boundary.

Parameter window: 350-520 $^{\circ}\text{C}$, 1-10 h, Ar/vacuum;

350-420 $^{\circ}\text{C}$: promote short-range order \rightarrow nanocrystal nucleation;

420-520 $^{\circ}\text{C}$: controlled growth and dispersion of nano-extrusion (to prevent coarsening and continuity);

During this period, the temperature can be increased in stages and multiple short insulation to "repair the dot matrix without excessive growth".

Characterization: XRD observation of amorphous to crystallization transformation; TEM/EDS observation of nano precipitation size (5-50 nm) and distribution.

(5) SPS densifying

Mold: graphite mold + graphite paper lining; vacuum or Ar.

Typical parameters: 560-660 $^{\circ}\text{C}$, 40-60 MPa, 3-6 min, heating 50-100 $^{\circ}\text{C}\cdot\text{min}^{-1}$

Strategy: The lower temperature + short insulation is adopted to retain the nano/sub-micron hierarchical structure constructed by annealing and avoid abnormal grain growth and second phase continuity.

Objective: The relative density should be $\geq 95-98\%$, the pores are small and not connected, and the interface is clean.

(6) Post-processing and electrothermal transport characterization

Optional reannealing at 450-520 $^{\circ}\text{C}$ / 2-6 h to fine-tune defects and interface barriers;

Complete density, SEM/TEM, Hall, Seebeck $\rho(T)\kappa(T)$, and whole process quality control.

2.3.2 Mechanism Characteristics and Microstructural Evolution

High cold speed effect: rapid solidification inhibits element deposition and coarse dendrite, forming fine equiaxed crystals or even amorphous/saturated solid solution, which reserves the starting point of nanostructure for subsequent "low temperature and short time" densification.

Induced dispersion precipitation by annealing: within the range of 350-520 $^{\circ}\text{C}$, nano-scale Mg or Sb enriched dispersion particles are precipitated in κ_L the matrix to construct multi-scale phonon scattering channels, which significantly reduces the energy loss;

Interface barrier/band regulation: The band material is derived from the non-equilibrium state, and the component gradient and interface states formed during annealing and SPS can produce weak barriers, which are expected to improve the selectivity of low and medium energy carriers and improve the power factor. However, the barrier is too strong to damage the mobility, so window control is needed.

2.3.3 Key Parameters and Process Control Points

Oxidation and surface film: the strip has a large specific surface area, inert environment throughout the process, rapid transfer and sealed preservation; before SPS, light Ar gas/low energy ion cleaning or short time pre-etching can be done to remove the film.

Non-equilibrium residual: after XRD identification, it can be eliminated by segmented annealing; the peak temperature of SPS should not be too low, otherwise the residual phase will generate transport scattering; too high will cause coarsening.

Thickness/Grain size coordination: increasing wheel speed and reducing injection pressure can reduce the thickness and increase the cooling speed; but too thin leads to breakage and difficulty in collection.

Mg volatilization and loss: control the melt overheating and injection time; small nozzle-wheel gap, short SPS insulation can help to suppress the loss.

Nodular/blocked nozzle: appropriately increase the superheat (≤ 150 °C), select BN lining and polished nozzle, and maintain a stable jet.

2.3.4 Common Failure Modes and Countermeasures

Black spots on the surface of the strip/oxidation → decreased migration rate

Countermeasures: higher purity Ar, shorter exposure, add the aforementioned pre-annealing/cleaning steps; discard severely oxidized batches.

Discontinuous and porous strips → Difficult to densify

Countermeasures: reduce the wheel speed or increase the injection pressure; optimize the nozzle-wheel gap and melt viscosity (fine-tuning temperature).

Non-equilibrium (amorphous residue) ρ_{excess} → increase

Countermeasures: increase the upper limit of annealing time or temperature, but the coarsening must be strictly controlled; if necessary, secondary segmented annealing.

Abnormal grain growth (SPS or overannealing) → Layer scattering attenuation

Strategy: low temperature + short insulation SPS strategy; annealing is carried out in multiple short times.

2.3.5 Quality Control and Baseline Indicators (Recommendations)

XRD: The main phase has high purity and weak residual non-equilibrium phase after annealing; compared with the traditional solid phase method, the peak half height width is larger (nanocrystal/microstrain).

Microscopic: 50 nm-1 μm grains are the main, 5-50 nm dispersed and uniformly distributed; pores are small and not connected.

Body density: Archimedes method $\geq 95-98\%$;

Electricity transport κ_L : lower than the conventional solid phase/SPS baseline while maintaining comparable mobility and appropriate carrier concentration.

2.3.6 Safety and Amplification Notes

Mg melt is combustible: open flame and oxygen leakage are prohibited; inert protective chamber and anti-backfire device are used; operators wear flame retardant protective equipment.

Spray belt equipment: copper wheel surface polishing, degreasing; nozzle and pipeline regular inspection to prevent blockage; set overflow/pressure relief valve.

Batch consistency: thick fluctuation and local oxidation are easy to lead to batch difference. Improve online monitoring and SPC (statistical process control), and leave samples and records by roll/batch.

2.3.7 Method Characteristics (Refinement)

High cooling rate and initial nanostructure friendly: fine equiaxed crystals/amorphous or supersaturated κ_L solid solution can be obtained in one molding, which is a low temperature and short time for densification and low foundation.

The "dispersion release + crystal boundary" hierarchical scattering can be constructed: after controlled annealing, a multi-scale κ_L phonon scattering network is formed to reduce without significantly sacrificing the mobility.

Band and interface tunability: The non-equilibrium starting point leads to an engineeringable interface barrier/band bending

Challenges and countermeasures are clear: surface oxidation, non-equilibrium phase residue and thickness consistency are the key pain points -- which can be effectively avoided by high purity inert atmosphere + segmented annealing + parameter windowing (wheel speed/gap/pressure) + short time SPS.

Applicability: It is feasible for Mg-Sb brittle compounds, but the window is narrow, and strict atmospheric and temperature control are required.

2.4 Solvent/Solids Salt Assisted Synthesis and Crystal Growth

The purpose of the process is to realize the dissolution-diffusion-redeposition/precipitation of Mg-Sb system in the temperature zone below the intrinsic melting point, and to prepare high quality single crystal or quasi single crystal for the separation of crystal anisotropy and interface/boundary effect, so as to serve the intrinsic study of "band-scattering mechanism-macroscopic ZT".

2.4.1 Process Route and Parameter Window

A. Metal Self-flux method (recommended for millimetre-scale single crystals)

Formulation and Loading: Using magnesium in excess by 200-500 at.% as the self-solvent (with an example $3/2$ molar ratio of Mg:Sb = 10-30:1, target phase MgSb), the material is loaded into a Ta-lined crucible (sealed with an argon arc weld) and then placed in a quartz outer tube under an Ar pressure of 0.2-0.5 atm.

Heating and homogenization: 720-860 °C/10-24 h complete melting and homogenization (overheating 50-150 °C relative to the liquid phase line).

Nucleation and growth: slow cooling -1 to 560-620 °C at 0.5-3.0 °C ·h for 10-30 h to promote preferential growth (temperature gradient of 5-15 °C can be set to achieve directional growth).

Pour/centrifuge to remove excess Mg flux: Pour or heat centrifuge at 520-580 °C to remove excess Mg flux; cool to room temperature.

Post-treatment: The surface flux is rapidly cleaned in a glove box with dry ethanol/ethyl acetate, followed by vacuum drying. If necessary, annealing at 400–500 °C for 2–6 h is performed to relieve stress and improve orderliness.

B. Molten salt (halide eutectic) approach (suitable for low temperature, batch fine crystals/plates)

Salt system selection: LiCl-KCl eutectic (melting point ≈ 352 °C) or CaCl-NaCl-KCl deep eutectic (melting point $\approx 450-500$ °C). Salt: Reactant (mass ratio) 5-10:1.

Reactor: AlO/BN $2/3$ beaker is placed in a closed alloy pot or quartz tube (vacuum and Ar filling).

Reaction and crystallization: isothermal holding at 420-560 °C for 12-48 h; during which the temperature can be increased in stages (e.g., 450 °C for 12 h \rightarrow 520 °C for 12 h) to promote dissolution and recrystallization.

Separation and washing: After cooling to room temperature, mechanical separation is performed in a glove box. Salt is removed by ultrasonic treatment with anhydrous ethanol/isopropanol. A short time of minimal deionized water rinsing (optional) is followed by rapid vacuum drying to avoid oxidation.

Shape annealing: 420-480 °C/2-8 h annealing to improve crystallinity and regulate micro precipitation.

Note: Metal self-solvent is more conducive to obtaining millimeter-scale, plate-like single crystals; the molten salt method has a lower temperature and can produce a large number of 10-200 μm single crystals in a single batch, which is suitable for statistical and doping parameter scanning.

2.4.2 Mechanism Features and Microstructural Evolution

Activity and solubility regulation: flux/molten salt significantly reduces the effective activation energy and diffusion distance, so that Mg and Sb complete dissolution-diffusion-reprecipitation in the low temperature range, and inhibit the segregation of coarse crystals and dendrites.

Optimal morphology and anisotropy: The layered structure of MgSb (CaAlSi type) is easy to form plate-like crystals, which facilitates the decoupling of transport measurement along in-plane and out-of-plane.

Defects and intrinsic state control: Low temperature growth and subsequent annealing are beneficial to reduce dislocation/ vacancy complexes and stabilize the distribution of intrinsic point defects; excess Mg in self-solvent helps to suppress type V vacancy defects.

Doping accessibility: The introduction of doping sources such as Te/Se/Bi in the flux medium makes it easier to achieve uniform solid solution and shorten the diffusion time.

2.4.3 Key Parameters and Process Control Points

Mg volatilization/oxidation: the double-layer packaging of Ta inner crucible and quartz outer envelope tube is preferred; the overheating should be controlled within 150 °C; the whole process is inert atmosphere and pre-drying.

Residual flux and secondary phase: self-solvent is easy to leave Mg/ rich Mg phase, which needs to be hot poured at 520-580 °C; surface residue should be quickly cleaned with mild organic solvent to avoid strong acid and alkali corrosion.

Hygroscopicity of salt water: LiCl₂/KCl/CaCl is easy to absorb moisture, so it should be placed in a glove box. Prioritize anhydrous alcohol for salt washing; if water is necessary, the time should be as short as possible and vacuum drying should be done immediately.

Cooling rate: too fast is easy to form fine crystals with multiple nucleation, too slow is easy to coarsen and induce macroscopic segregation; typical 0.5–3.0 °C·h⁻¹.

Temperature gradient: a 5-15 °C gradient in the 1-3 cm region is conducive to oriented growth; a large gradient is easy to produce thermal stress cracks.

Impurity introduction: Metal flux (e.g., Sn/Bi) will be unintentionally doped and change the carrier type/concentration; Mg self-solvent or halide molten salt should be preferred for intrinsic transport studies.

2.4.4 Common Failure Modes and Countermeasures

Crystal inclusions flux/salt → Abnormal low temperature electrical transport

Countermeasures: optimize the hot pouring temperature, prolong the insulation and clarification time; ultrasonic + short time gentle cleaning, secondary annealing if necessary.

Oxidation and blackening/surface roughness → decreased migration rate

Countermeasures: operate with gloves throughout the process; dry and package immediately after cleaning.

Small size/orientation difference

Countermeasures: reduce supersaturation (increase the initial temperature or slightly reduce the cooling rate), introduce a temperature gradient, and reduce the heterogeneous nucleation point (polish the crucible).

Crystallization cracking (thermal stress)

Countermeasures: Set a buffer insulation step (e.g., 680→640→600 °C, 6-12 h per step), and control the cooling rate ≤ 2 °C·h⁻¹.

2.4.5 Quality Control and Characterization Baseline

Phase purity and orientation: single crystal XRD/laue spots are clear; after powderization, XRD has no obvious flux/salt residue peak;

Chemical measurement: ICP-OES/EPMA close to the design value;

Appearance: plate-like, neat edges, no significant step peeling and through cracks;

Transport: in-plane/extrapolation σ_{Sc} , show reasonable anisotropy; Hall mobility and carrier concentration are stable, batch difference is controllable.

2.4.6 Safety and Amplification Notes

Mg melt/powder is combustible: no water and fire, wear flame retardant protection;

Halide salt corrosion and moisture absorption: protect the metal parts before contact, use corrosion-resistant containers and operate with low dew point;

Centrifugation/dumping flux: pay attention to anti-splash and stress crack in high temperature operation;

Batch consistency: Establish SPC (statistical process control): record salt ratio, cooling rate, flux temperature, crystal size distribution and O content.

2.4.7 Method Characteristics (Refinement)

Low temperature controlled crystallization: crystal growth is achieved in the temperature zone significantly lower than the melting point, which reduces defects and stress, and is conducive to the study of intrinsic transport.

Anisotropy friendly: it is easy to obtain plate-like single crystal, which facilitates the measurement and band/scattering mechanism analysis along different crystal directions.

Convenient impurity and defect engineering: uniform solid solution and wide control window of point defects in flux/molten salt environment are suitable for systematic scanning.

The window is narrow and the process threshold is high: strict requirements on water and oxygen control, temperature range/gradient, and flux removal; there is a risk of unintentional doping of metal flux, which needs to be cross-verified with chemical analysis and electrical transport data.

It can be complementary to 2.1-2.3: single crystal is used for intrinsic parameter calibration and mechanism study, and sintered block is used for engineering performance optimization, which together support the interpretable improvement of ZT.

3. Main Methods to Improve the Performance of N-type MgSb based Materials

3.1 Carrier and Band Engineering: Improving $S^2\sigma$ the Power Factor

3.1.1 Donor/Acceptor Defects and Fermi Level Control

The common Mg vacancy and anti-defects in the Mg-Sb system can lead to the intrinsic p-type tendency. To achieve a stable n-type, it is necessary to:

Synthesis thermodynamic window: Mg enrichment conditions are used to inhibit the thermodynamic generation of host defects by rapid densification;

Donor doping strategy: Sb equivalent heteroatoms or Mg transition/REEs are introduced to introduce 10^{19} cm^{-3} electrons, and the carrier concentration is adjusted to the optimal range of levels;

Defect recombination: Through element ratio and annealing process, beneficial defects (such as donor-vacancy recombination) are promoted to exist stably, and dissociation energy and dissociation scattering are reduced.

Reference: SnTe-based materials significantly enhance power factors by adjusting Fermi levels through Na/K doping and utilizing band convergence [1]. Hui Mei Pang, Hua Cai Wang. Research Progress of Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. Zintl phase achieves "natural band edge designability" with constraints on valence bonds, anion framework, and valence electron count [3]. Mi Juan Luo. Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite with SnTe-Based Alloys: Microstructure and Thermoelectric Properties [D]. Harbin Institute of Technology, 2022. This provides insights for doping selection and valence electron counting in Mg-Sb systems.

3.1.2 Band Convergence and Valley Merger

For n-type Mg-Sb alloys, the fundamental strategy for achieving band convergence and valley degeneracy lies in: without significantly sacrificing mobility, utilizing electron-sharing alloying to reduce the conduction band valley energy gap while enhancing effective degeneracy. Simultaneously,

the random alloy potential field is employed to enhance mid-to-high frequency phonon scattering, thereby realizing the synergy between "high power factor" and "low lattice thermal conductivity". The specific feasible pathways are as follows:

Sb-site isoelectronic alloying (Bi-priority): construct $\text{Mg}_{1-x}\text{Sb}_x\text{Bi}$ solid solution, adjust the conduction band structure through lattice distortion and chemical pressure, and promote the energy valley closer; at the same time, introduce mild random alloy scattering to achieve the decoupling of "good electric-low heat".

Combined Regulation of Fermi Level and Carrier Concentration: Under the synthesis window enriched with magnesium, acceptor-type intrinsic defects are suppressed. By introducing trace donors (such as trace donors at the Sb/Se/Te positions or light doping of La/Ce at the Mg position), the Fermi level is fine-tuned to bring carrier concentration into the optimal power factor range, thereby avoiding dissociation scattering caused by deep energy levels.

Interface barrier and mobility protection: Fine grains can improve the interface density, but it is necessary to promote the interface rearrangement and purification (low oxygen and low impurity) through subsequent annealing to maintain low barrier and clean interface; when necessary, control the volume fraction and size of the second phase to prevent the loss of mobility caused by continuous or coarsening.

Process coordination: It is recommended to use SSR/MA (mechanical alloying) + SPS for the non-equilibrium-rapid densification route, first to obtain a uniform solid solution and a "scaffold" of nano/substructures, and then to stabilize the degree of alloying and interface quality through medium temperature annealing, so as to realize the superposition of cross-band phonon scattering without excessive reduction of mobility.

Methodological References but Refinement within the System: The collaborative optimization experience regarding "band convergence + random alloy scattering + shallow donor fine-tuning" observed in SnTe, Zintl phases, and Mo-Se-Te solid solutions can serve as strategic inspiration. However, for Mg-Sb systems, the core approach should focus on electron alloying processes like Sb→Bi, shallow donor trace regulation, and Mg enrichment techniques. Parameter screening and robustness evaluation should be conducted around three key elements: carrier mobility protection, phonon multi-scale scattering, and Fermi level positioning.

3.1.3 Migration Rate Preservation: Synergistic Management of Interfacial Barrier and Ionization Scattering

Fine grains and high dislocation κ_L density can reduce but easily introduce interface barrier, reducing electron mobility. It is necessary to set the parameter window of "medium refinement, low barrier, weak dissociation" among grain size, interface quality and point defect concentration:

Control oxygen/impurities to reduce Coulomb scattering;

Use low energy interface (annealing promotes rearrangement) to reduce the barrier height;

Deep energy levels are suppressed by electron/shallow donor doping.

3.2 Multiscale Lattice Thermal Conductivity κ_L Regulation: Suppression

3.2.1 Random Solid Solution and Mass-force Constant Perturbations

The quality and bond strength differences caused by element substitution establish medium/high-frequency phonon scattering channels. Studies on the MoSeTe and SnTe systems (1) Pang Huimei, Wang Huaicai. Research Progress of Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. (4) Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of Thermoelectric Transport Properties in Nb-Doped $\text{Mo}_{1-x}\text{W}_x\text{SeTe}$ Solids κ_L [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. (5) Zhou Xingyuan. Study on Electrowarm Transport Optimization of MoSeTe-Based Solids and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020.) demonstrate that alloying significantly suppresses these effects while remaining compatible with band engineering approaches.

3.2.2 Nano/micron-level Scattering

Mechanical alloying and rapid quenching can induce nanocrystalline structures and dislocation cell configurations. Through SPS (Superparametric Supercomputer System) and annealing refinement, a hierarchical scattering network of grain boundaries, substructures, and precipitates can be formed, enabling superposition of cross-band phonon scattering ([7]). Ran Guang, Zhou Jing'en, Xi Shengqi. Study on the Mechanism of Amorphous Formation via Mechanical Alloying [J]. Metal Heat Treatment, 2005(11):13-16. Ji Hanrong. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998(01):44-49. Jia Dechang, Zhou Yu, Lei Tingquan. Advances in Mechanical Alloying and Its Applications in Aluminum Alloys and Alumina-Based Composites [J]. Aerospace Materials Processing, 1996(01):1-9+16. Continuous growth or coarsening of secondary phases should be avoided to prevent degradation.

3.2.3 Dispersion Precipitation and Second Phase Interface Design

Drawing on the semi-Hall system methodology, a second phase with low volume fraction, nanoscale dimensions, clean interface, and band alignment-friendly properties can effectively scatter mid-to-low frequency phonons without significantly reducing mobility. By controlling precipitation density and size distribution through annealing kinetics, this approach achieves "soft interface and strong scattering" characteristics.

3.2.4 Lattice Dynamics and Indexation Design

Using key parameters such as Debye temperature, sound velocity, and phonon lifetime, this study integrates first-principles data with empirical principles (refer to the design approach for low lattice thermal conductivity spinel selenides [2] by Yan Li. Design and κ_L Thermoelectric Properties of Low Lattice Thermal Conductivity Spinel Selenides [D], Henan University, 2024) to provide a "low prior" framework for alloying strategies in Mg-Sb systems.

3.3 Experience Transfer: The Portability of Cross-system Optimization Strategies

From SnTe to Mg-Sb: The "Electrothermal Decoupling" Strategy of Band Convergence and Point Defect Engineering (Reference [1] Hui Mei Pang, Hua-Cai Wang. Research Progress on Tin Selenide-Based Thermoelectric Materials. Science Bulletin, 2025,70(06):645-654); From MoSeTe to Mg-Sb: Paradigm of Transport Synergy Optimization via Random Solid Solution/Solution Scattering and Trace Doping with Transition Metals (Reference [4] Xuan Zhou, Wei Liu, Cheng Zhang, et al. Thermal-Electronic Transport Performance Optimization of Nb-Doped Mo_{1-x}W_xSeTe Solid Solution. Journal of Inorganic Materials, 2020,35(12):1373-1382. Reference [5] Xuan Zhou. Study on Electrothermal Transport Optimization of MoSeTe-Based Solid Solution and Wurtzite Semimetal NbP. Wuhan University of Technology, 2020); From Zintl Phase to Mg-Sb: Impact of Valence Electron Counting and Anion Framework on Band Edges and Effective Carrier Mass (Reference [3] Min-Juan Luo. Structure-Performance Relationship of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds Composite with SnTe-Based Alloys. Harbin Institute of Technology, 2022). From MA/Fire Metallurgy to Mg-Sb: Providing Structural "Scaffold" for Hierarchical Scattering through Mechanical Alloying's Non-Equilibrium Structure (Reference [7] Ran Guang, Zhou Jing'en, Xi Shengqi. Study on Amorphous Mechanism Preparation by Mechanical Alloying [J]. Metal Heat Treatment, 2005, (11):13-16. [8] Ji Hanrong. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998, (01):44-49. [9] Jia Dechang, Zhou Yu, Lei Tingquan. Advances in Mechanical Alloying and Its Applications in Alloys and Alumina-Based Composites [J]. Aerospace Materials Processing, 1996, (01):1-9+16.). From SnTe to Mg-Sb: The "Electrothermal Decoupling" Strategy of Band Convergence and Point Defect Engineering ([1] Hui Mei Pang, Hua-Cai Wang. Research Progress of Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654.); From MoSeTe to Mg-Sb: The Paradigm of Random Solid Solution/Solution Dispersity and Trace Doping for Transport Synergy Optimization ([4] Xuan Yuan Zhou, Wei Liu, Cheng Zhang, et al. Thermal-Electronic Transport Performance Optimization of Nb-Doped Mo_{1-x}W_xSeTe Solid Solution [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Xuan Yuan

Zhou. Electrothermal Transport Optimization of MoSeTe-Based Solid Solution and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020.); From Zintl Phase to Mg-Sb: Effect of Valence Electron Counting and Anion Framework on Band Edges and Effective Carrier Mass ([3] Min-Juan Luo. Structure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds Composite with SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022.); From MA/Fire Metallurgy to Mg-Sb: Providing Structural "Scaffold" for Hierarchical Scattering through Mechanical Alloying's Non-Equilibrium Structure (Reference [7]). Ran Guang, Zhou Jing'en, Xi Shengqi. Study on Amorphous Mechanism Preparation by Mechanical Alloying [J]. Metal Heat Treatment, 2005(11):13-16. Ji Hanrong. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998(01):44-49. Jia Dechang, Zhou Yu, Lei Tingquan. Advances in Mechanical Alloying and Its Applications in Aluminum Alloys and Alumina-Based Composites [J]. Aerospace Materials Technology, 1996(01):1-9+16.

From SnTe to Mg-Sb: The "Electrothermal Decoupling" Strategy of Band Convergence and Point Defect Engineering (1) Hui Mei Pang, Hua-Cai Wang. Research Progress on Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. (2) From MoSeTe to Mg-Sb: The Paradigm of Random Solid Solution/Solution Dispersity and Trace Doping for Transport Synergy Optimization (4) Xuan Yuan Zhou, Wei Liu, Cheng Zhang, et al. Thermal-Electronic Transport Performance Optimization of Nb-Doped Mo_{1-x}W_xSeTe Solid Solution [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Xuan Yuan Zhou. Study on Electrothermal Transport Optimization of MoSeTe-Based Solid Solution and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020. (3) From Zintl Phase to Mg-Sb: Effect of Valence Electron Counting and Anion Framework on Band Edges and Effective Carrier Mass [3] Minjuan Luo. Structure-Property Relationship of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds Composite with SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. (4) From MA/Fire Metallurgy to Mg-Sb: Providing Structural "Scaffold" for Hierarchical Scattering through Mechanical Alloying's Non-Equilibrium Structure (Reference [7]) Ran Guang, Zhou Jing'en, Xi Shengqi. Study on Amorphous Mechanism Preparation via Mechanical Alloying [J]. Metal Heat Treatment, 2005(11):13-16. [8] Ji Hanrong. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998(01):44-49. [9] Jia Dechang, Zhou Yu, Lei Tingquan. Mechanical Alloying and Its Application Progress in Alloys and Alumina-Based Composites [J]. Aerospace Materials Technology, 1996(01):1-9+16.).

4. Focus on the Performance Improvement and Application Prospect of this Thermoelectric Material

4.1 Performance Improvement of N-type Mg-Sb based Thermoelectric Materials (Methodological Transfer Combined with Literature)

4.1.1 The Dual Objectives of "High Power and Low Heat": Decoupling of Power Factor and Lattice Thermal Conductivity

To achieve high ZT in room temperature-medium temperature region, the key lies in improving $S^2\sigma\kappa_L$ power factor without sacrificing mobility, and suppressing lattice thermal conductivity through multi-scale scattering. Existing systems have given clear migration strategies:

(1) Band Convergence + Defect Engineering: The SnTe-based research system demonstrates that increasing effective state density and maintaining mobility through band valley narrowing $\kappa_L\kappa_L(2 \ 2 \ 1-x \ x)$ and Fermi level modulation significantly enhances power factor. This approach, combined with point defects/multi-scale scattering reduction strategies, is validated in [1] Hui-Mei Pang and Hua-Cai Wang. Research Progress on Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. (2) Lattice Dynamics Prioritization for Low Thermal Conductivity: Systematic studies on spinel selenides emphasize using Debye temperature, acoustic velocity, and other parameters to guide material design and optimize alloying directions for natural suppression [2] Hui-Mei Pang and Hua-Cai Wang. Research Progress on Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. (3) Valence Electron Counting

and Framework Regulation in Zintl Phases: Experimental studies on Zintl phase Ca(Yb)MgBi composites demonstrate that the "valence electron counting-anion framework" mechanism enables precise band edge modulation without significant mobility degradation [3] Luo Mijuan. Structural and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds in SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. (4) Synergistic Effect of Random Solid Solution and Light Doping: Research on MoWSeTe/Nb Solid Solutions reveals that mass/force constant perturbations combined with light transition metal doping simultaneously modulate carrier and phonon scattering channels, achieving "electric-thermal synergy optimization" [4] Zhou Xingyuan, Liu Wei, Zhang Cheng et al. Thermal-Electric Transport Optimization of Nb-Doped Mo_{1-x}W_xSeTe Solids [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Electrothermal Transport Optimization of MoSeTe-Based Solids and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020.(1) Band Convergence + Defect Engineering: The SnTe-based research system demonstrates that increasing effective state density and maintaining mobility through band valley narrowing and Fermi level modulation significantly enhances the power factor. This is achieved in conjunction with a paradigm combining point defects/multi-scale scattering reduction (Pang Huimei & Wang Huaicai, "Research Progress on Tin Selenide-Based Thermoelectric Materials", Science Bulletin, 2025,70(06):645-654). (2) Lattice Dynamics Prioritization for Low Thermal Conductivity: Systematic studies on spinel selenides emphasize using indicators such as Debye temperature, acoustic velocity, and other metrics to guide material design and optimize alloying directions to naturally suppress thermal conductivity [Pang Huimei & Wang Huaicai, "Research Progress on Tin Selenide-Based Thermoelectric Materials", Science Bulletin, 2025,70(06):645-654]. (3) Valence Electron Counting and Framework Regulation in Zintl Phases: Experimental studies on Zintl phase Ca(Yb)MgBi composites demonstrate that the "valence electron counting-anion framework" mechanism enables precise band edge modulation without significant mobility degradation (Luo Mijuan et al., 2022, [3]). (4) Synergistic Effect of Random Solid Solution and Light Doping: Research on MoWSeTe/Nb solid solutions reveals that mass/force constant perturbations combined with light transition metal doping simultaneously modulate carrier and phonon scattering channels, achieving "electric-thermal synergy optimization" (Zhou Xingyuan et al., 2020, [4]). The thermal-electrical transport properties of Nb-doped Mo_{1-x}W_xSeTe solid solutions were optimized through mass/force constant perturbations and light transition metal doping. (1) Band Convergence + Defect Engineering: The SnTe-based research system demonstrates that increasing effective state density and maintaining mobility through band valley narrowing and Fermi level modulation significantly enhances the power factor. This is achieved in conjunction with a paradigm combining point defects/multi-scale scattering reduction (Pang Huimei & Wang Huaicai, 2025, Science Bulletin, 70(06):645-654). (2) Lattice Dynamics Prioritization for Low Thermal Conductivity: Systematic studies on spinel selenides emphasize using indicators such as Debye temperature, acoustic velocity, and other metrics to guide material design and optimize alloying directions for natural suppression [Pang Huimei & Wang Huaicai, 2025, Science Bulletin, 70(06):645-654]. (3) Valence Electron Counting and Framework Regulation in Zintl Phases: Experimental studies on Zintl phase Ca(Yb)MgBi composites demonstrate that the "valence electron counting-anion framework" mechanism enables precise band edge modulation without significant mobility degradation [3] Luo Mijuan. Structural and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds in SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. (4) Synergistic Effect of Random Solid Solution and Light Doping: Research on MoWSeTe/Nb-doped solid solutions reveals that mass/force constant perturbations and light transition metal doping simultaneously modulate carrier and phonon scattering channels, achieving "electric-thermal synergy optimization" [4] Zhou Xingyuan, Liu Wei, Zhang Cheng et al. Thermal-Electric Transport Optimization of Nb-Doped Mo_{1-x}W_xSeTe Solid Solutions [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Study on Electric-Thermal Transport Optimization of MoSeTe-Based Solid Solutions and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020.(1) Band Convergence + Defect Engineering: The SnTe-based research system demonstrates

that increasing effective state density and maintaining mobility through band valley narrowing and Fermi level modulation significantly enhances the power factor. This is achieved in conjunction with point defects/multi-scale scattering reduction (Pang Huimei & Wang Huaicai, "Research Progress on Tin Selenide-Based Thermoelectric Materials", Science Bulletin, 2025,70(06):645-654). (2) Lattice Dynamics Prioritization for Low Thermal Conductivity: Systematic studies on spinel selenides emphasize using Debye temperature, acoustic velocity, and other parameters to guide material design and optimize alloying directions for natural suppression [Pang Huimei & Wang Huaicai, "Research Progress on Tin Selenide-Based Thermoelectric Materials", Science Bulletin, 2025,70(06):645-654]. (3) Valence Electron Counting and Framework Regulation in Zintl Phases: Experimental studies on Zintl phase Ca(Yb)MgBi composites demonstrate that the framework of valence electron counting and anion skeleton enables precise band edge control without significantly degrading mobility (Luo Mijuan et al., 2022, [3]). (4) Synergistic Effect of Random Solid Solution and Light Doping: Research on MoWSeTe/Nb solid solutions reveals that mass/force constant perturbations and light transition metal doping simultaneously influence carrier and phonon scattering channels, achieving "electric-thermal synergy optimization" (Zhou Xingyuan et al., 2020, [4]). The thermal-electrical transport properties of Nb-doped Mo_{1-x}W_xSeTe solid solutions were optimized through mass/force constant perturbations and light transition metal doping (Zhou Xingyuan et al., 2020, [5]).

4.1.2 Migration and Landing of N-type Mg-Sb:

(1) Carrier Regulation: The synthesis employs Mg-enriched conditions to suppress host-type intrinsic defects $n\mu S\sigma$. By utilizing the Hall-Pisarenko relationship inversion and optimal coupling range, this approach avoids dissociation scattering caused by deep energy levels (referencing the Fermi level fine-tuning strategy in SnTe [1] by Hui Mei Pang and Hua-Cai Wang. Research Progress on Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. and the "valence electron counting" principle for Zintl phases [3] by Ji Juan Luo. Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds Composite with SnTe-Based Alloys: Microstructure and Thermoelectric Properties [D]. Harbin Institute of Technology, 2022.). (2) Band Engineering and Valley Singularity: The light alloying of equivalent heteroatoms induces conduction band singularity to enhance effective mass and state density while preserving mobility (inspired by multi-valley parallelism in SnTe [1]). Pang Huimei & Wang Huaicai. Research Progress on Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. Zhou Xingyuan et al. Light-Tuned Alloy Strategies for MoSeTe [4]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Optimization of Electrolocal Heat Transfer in MoSeTe-Based Solvent and Wurtzite Semimetal NbP [D]. Wuhan University of Technology, 2020. (3) Migration Protection: The design adopts "low barrier, soft interface, clean interface" for refined grain boundaries and second phases, controlling oxygen/impurities. When necessary, annealing is employed to promote interface reorganization. This approach balances the mild enhancement and maintenance under energy filtering effects (consistent with the "mild filtering + low barrier" concept in SnTe and Zintl phase literature [1]). Pang Huimei & Wang Huaicai. Research Progress of Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [2] Pang Huimei & Wang Huaicai. Research Progress of Tin Selenide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite with SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022.). (4) Multiscale Scattering Mechanisms: The medium-to-high frequency range is initially covered by point defects/solution scattering. Subsequently, a cross-frequency superposition scattering network is formed through nanoscale precipitation, dislocation cells, and grain boundaries (MoSeTe solution + Nb doping provides "random solution × light doping" synergistic evidence [4] Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of thermoelectric transport properties in Nb-doped Mo_{1-x}W_xSeTe solution [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Study on optimization of electrothermal transport in MoSeTe-based solutions and Weyl semimetal NbP [D]. Wuhan University of Technology, 2020.). (5) Non-equilibrium Process as Structural "Scaffold": Mechanical Alloying (MA) + Discharge Plasma Sintering (SPS) can form nanocrystalline/high

dislocation density substructures at lower temperatures, achieving hierarchical scattering while shortening reaction pathways and enhancing phase homogeneity. The parallel implementation of MA/SSR dual routes, combined with Mg compensation and atmosphere/heating curve optimization, reduces risks of Mg volatilization and pore formation (the non-equilibrium characteristics of MA are comparable to the structure refinement patterns in Al-based/composite materials [7]). Ran Guang, Zhou Jing'en, Xi Shengqi. Research on Amorphous Mechanism Preparation by Mechanical Alloying [J]. Metal Heat Treatment, 2005, (11):13-16. [8] Hanrong Ji. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998, (01):44-49. [9] Jia Dechang, Zhou Yu, Lei Tingquan. Advances in Mechanical Alloying and Its Applications in Alloys and Al-Based Composites [J]. Aerospace Materials Processing, 1996, (01):1-9+16. (6) Matching and process reference of p/n end: The powder metallurgy experience of MgAgSb based alloy has reference value for p-end matching, modularization and enlarged manufacturing, which can ensure the resistivity at the matching end and improve the module filling factor [6].

4.1.3 Operable Verification Matrix

(1) The three steps of baseline, band and scattering:

- ① Establishment $S(T), \sigma(T), \kappa(T)$ of baseline samples;
- ② Light doping screening of $n\mu$ equivalent heterogeneous atoms--Pareto frontier;
- ③ By superimposing annealing/diffusion precipitation κ_L and rapid quenching on the optimal composition, a measurable reduction of $\geq 30\%$ was achieved.

(2) Robustness evaluation: Thermal cycling (300–650 K) and isothermal aging (600–650 K) showed target performance drift $\leq 10\%$. Comparative analysis of interfacial reaction layer thickness and contact resistance variations established a "composition-process-stability" mapping (consistent with accelerated life assessment pathways for SnTe/Zintl/solution system [1] Pang Huimei, Wang Huaicai. Research Progress of Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [2] Pang Huimei, Wang Huaicai. Research Progress of Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. [4] Zhou Xingyuan, Liu Wei, Zhang Cheng et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solids [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solids and Wurtzite Semi-metal NbP [D]. Wuhan University of Technology, 2020.

4.2 Application Prospect and Engineering Route

4.2.1 Temperature Zone Positioning and Scene Fit

The n-type Mg-Sb thermoelectric material achieves temperature range locking between room and medium temperatures (approximately 300–700 K), overlapping closely with low-temperature zones in industrial waste heat sources (steam pipelines, kiln ₂ ₃ exteriors, flues) and transportation electromechanical systems. It also demonstrates potential for self-powered sensing in low- ΔT scenarios like data centers and communication cabinets. Compared to high-Te-based BiTe/SnTe systems, Mg/Sb compounds offer advantages in resource abundance and environmental friendliness regarding scalability and compliance (see cost and element accessibility discussions in the SnTe system review [1] by Pang Huimei and Wang Huaicai, Science Bulletin, 2025,70(06):645-654; spinel selenides and Zintl phase studies also emphasize comprehensive material-environment-cost trade-offs [2] by Pang Huimei and Wang Huaicai, Science Bulletin, 2025,70(06):645-654; [3] Luo Mijuan, Structural Organization and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compounds Composite with SnTe-Based Alloys [D], Harbin Institute of Technology, 2022).

4.2.2 Modular Key: p/n Matching, Metallization and Thermal Management

(1) P/N-end Matching: It is recommended to prioritize pairing with Type P MgAgSb systems or other room-temperature-to-mid-temperature window Type P materials. Match the resistivity and optimize the leg length/area/spacing ratio to enhance the module's filling factor and output. The microstructure-transport-tempering experience of MgAgSb can be directly referenced [6] Liu Zihang. Microstructure and Thermoelectric Properties of MgAgSb-Based Alloys [J]. Harbin Institute of Technology, 2017.

(2) Electrode and Diffusion Barrier: A layered connection using Ni/Cr barrier layer + Cu/Ag conductor is adopted to suppress element inter-diffusion and contact resistance drift, maintaining long-term stability (Long-term stability assessment of SnTe/Zintl/solution matrix all emphasizes interface reaction layer control [1] Pang Huimei, Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Structure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite with SnTe-Based Alloy [D]. Harbin Institute of Technology, 2022. [4] Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solvent [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solvent and Wurtzinger Halfmetal NbP [D]. Wuhan University of Technology, 2020.). (3) Thermal Interface Material (TIM) and Thermal Management: Under specified ΔT and heat flux density conditions, the module must be integrated with a heat exchanger/heat sink to maximize effective temperature difference and minimize thermal bypass losses. System-level performance is comprehensively evaluated using $mW \cdot cm^{-2}$ output and $\$/W$ cost (referencing the standard evaluation system for multi-system modular practices [1]). Pang Huimei & Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [2] Pang Huimei & Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. [4] Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solvent [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solvents and Wurtzite Semi-metallic NbP [D]. Wuhan University of Technology, 2020.

4.2.3 Process Amplification and Consistency

(1) From Laboratory to Pilot Production: The SSR/MA + SPS route enables seamless progression from FAST/SPS scaling to hot pressing/mold molding and strip heat treatment. The powder homogenization effect of MA and the rapid densification characteristics of SPS share commonalities with Al-based/composite material scaling experience (References [7]: Ran Guang, Zhou Jing'en, Xi Shengqi. Research on Amorphous Mechanism Preparation via Mechanical Alloying [J]. Metal Heat Treatment, 2005(11):13-16; Hanrong Ji. Mechanical Alloying Technology in Solid-State Reactions [J]. Yunnan Metallurgy, 1998(01):44-49; Chang Jia, Zhou n, μ Yu, Lei Tingquan. Mechanical Alloying and Its Applications in Alloys and Al-Based Composites [J]. Aerospace Materials Technology, 1996(01):1-9+16). (2) Process Quality Control (PQC): Establish batch traceability and reduce sample dispersion by setting statistical control limits using XRD/Rietveld patterns, density, oxygen content, particle size distribution, and Hall parameters (as outlined in the literature on tin-sulfide-based thermoelectric materials emphasizing the "structure-transport-reproducibility" triad [1]). Pang Huimei and Wang Huacai. Research Progress on Tin Sulfide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [2] Pang Huimei and Wang Huacai. Research Progress on Tin Sulfide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022. [4] Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solvent [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382. [5] Zhou

Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solvent and Wurtzinger Halfmetal NbP [D]. Wuhan University of Technology, 2020.

4.2.4 Reliability and Life Cycle (LCA)

(1) Reliability: Conducted thermal cycling (300–650 K, ≥ 500 cycles), constant temperature aging (≥ 100 h), humidity/alkali-sulfur salt spray (scenario-specific), and mechanical vibration tests. Defect identification through cross-sectional electron microscopy and elemental analysis (revealing thickened reaction layers, pore migration, microcracks, etc.), establishing a closed-loop mechanism from doping to interface optimization and process refinement. [1] Pang Huimei & Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials. Science Bulletin, 2025,70(06):645–654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys. Harbin Institute of Technology, 2022. [4] Zhou Xingyuan, Liu Wei, Zhang Cheng et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solvent. Journal of Inorganic Materials, 2020,35(12):1373–1382. [5] Zhou Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solvents and Wurtzite Semi-metallic NbP. Wuhan University of Technology, 2020. (2) Life Cycle Assessment (LCA) and Supply Chain Resilience: Compared with high-tin formulations, Mg-Sb alloys inherently possess sustainable attributes in resource acquisition and environmental compliance, supporting large-scale deployment. [1] Pang Huimei & Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [2] Pang Huimei & Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654. [3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022.

4.2.5 Scenario Milestones and Evaluation Metrics

(1) Small Module Direct-Connect Verification: Test open-circuit voltage, internal resistance, maximum output power, and efficiency using $2 \times 2/3 \times 3$ chip arrays under $\Delta T = 100$ K conditions; (2) Platform-Level Demonstration: Install one demonstration unit on both the steam pipeline's outer wall and the heat sink's backside, recording $\text{mW} \cdot \text{cm}^{-2}$ power $ZT_{\text{peak}}ZT_{\text{avg}}$ density with thermal cycling performance retention rate $\geq 85\%$; (3) Engineering Indicators: The phased acceptance criteria are established by aligning material-level consistency and engineering-level stability (drift $\leq 10\%$, $\pm 7\%$ deviation) as stage acceptance standards (consistent with the multi-system "material-module-system" integrated evaluation framework in literature [1] Pang Huimei, Wang Huaicai. Research Progress on Tin Oxide-Based Thermoelectric Materials [J]. Science Bulletin, 2025,70(06):645-654.[3] Luo Mijuan. Microstructure and Thermoelectric Properties of Zintl Phase Ca(Yb)Mg₂Bi₂ Compound Composite SnTe-Based Alloys [D]. Harbin Institute of Technology, 2022.[4] Zhou Xingyuan, Liu Wei, Zhang Cheng, et al. Optimization of Thermoelectric Transport Properties in Nb-Doped Mo_{1-x}W_xSeTe Solvent [J]. Journal of Inorganic Materials, 2020,35(12):1373-1382.[5] Zhou Xingyuan. Optimization of Electrowarm Transport Properties in MoSeTe-Based Solvents and Wurtzite Semi-metallic NbP [D]. Wuhan University of Technology, 2020.[6] Liu Zihang. Microstructure and Thermoelectric Properties of MgAgSb-Based Alloys [D]. Harbin Institute of Technology, 2017).

5. Conclusion

This paper systematically reviews the latest research progress of N-type Mg₃Sb₂ -based thermoelectric materials in the low-temperature to medium-temperature range (300-700 K). As a new type of thermoelectric material that is rich in resources, low in cost and excellent in performance, Mg₃Sb₂ -based materials have shown great potential in improving thermoelectric conversion efficiency and promoting the large-scale application of thermoelectric devices.

References

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