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Recent Progress on Quaternary Copper -based Diamondoid Thermoelectric Materials

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bid mate **Abstract**: The rising concern on energy and environmental crises have sparked global interest in developing sustainable new energy and high -efficient energy conversion technologies. Thermoelectric technology has gained attention due to its potential for application in $\frac{4}{x}$ [w](#page-18-0)aste heat recovery and solid-state refrigeration. However, the application of traditional thermoelectric materials remains limited due to their expensive and toxic elemental composition. Recently, quaternary copper -based diamondoid materials have garnered significant interest due to their unique transport properties, high element abundance, and low toxicity . Many of these materials have demonstrated promising *ZT* value, positioning them as potential candidates for efficient thermoelectric applications . This paper summarizes the recent progress in copper -based quaternary diamondoid materials . We present a collection of research focused on optimizing electrical transport properties through carrier concentration tuning and band engineering , along with an overview of reducing thermal conductivity *via* microstructure enhanced phonon scattering . Finally, we analyze the current research bottlenecks in copper -based quaternary diamondoid thermoelectric materials and propose future research directions.

Keywords: quaternary Cu-based diamondoid materials, thermoelectric performance, carrier concentration, band engineering, microstructure

[17](#page-19-0) Introduction

The continuous rise in global energy demand and the depletion of unrenewable fossil fuels have made the development of sustainable new energy and high-efficiency

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energy conversion technologies become the worldwide topics. Research indicates that approximately 65% of energy produced in human activities is wasted and lost as heat^[1]. Thus, developing effective methods to recovery this waste heat is considered as a way to solve the energy problems. Thermoelectric materials^[2-4], based on the Seebeck effect, ca[n di](#page-20-0)rectly convert heat into electricity, and can also be used for solid state cooling. This makes them a promising tool for mitigating energy crises^[5]. However, the low energy conversion efficiency of thermoelectric materials limits their large-scale commercial applications^[6].

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belectric figure of merit ZT, $ZT = S^2 \sigma T /$.
oefficient, σ is electrical conductivity, T is
all conductivity, κ is latt Generall[y, th](#page-18-0)e performance of thermoelectric materials is mainly evaluated by the dimensionless thermoelectric figure of merit *ZT*, $ZT = S^2 \sigma T / \kappa_{tol} = S^2 \sigma T / (\kappa_e + \kappa_l)$, where *S* is Seebeck coefficient, σ is electrical conductivity, *T* is absolute temperature, κ_{e} is electronic thermal conductivity, κ_{i} is lattice thermal conductivity, and the sum of κ_e and κ_l is the total thermal conductivity of the material $\kappa_{\text{tol}}^{[7-9]}$. $PF = S^2 \sigma$, which is ⁴ power factor used to characterize the electrical transport performance of thermoelectric materials. Therefore, to improve the performance of thermoelectric materials, two main approaches are typically pursued: (1) optimizing the electrical properties; (2) reducing thermal conductivity^[10, 11]. However, because of the strong inherent coupling betwee[n el](#page-19-0)ectrical conductivity σ , Seebeck coefficient *S*, and thermal conductivity κ_{tol} , it is challenging to solely regulate these parameters to achieve high thermoelectric performance^[12]. For instance, increasing the carrier concentration can enhance σ , but this often reduces the *S* and increases κ _e, limiting the overall improvement in *ZT*. To overcome this, researchers employ various strategies to

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decouple these properties, aiming for enhanced thermoelectric efficiency.

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Instituted by Shi^[33] and Liu et al^[34].
Frials have attracted widespread attentio
en, a growing number of wide bandgap d
uch as CuIn Since the discovery of thermoelectric effect, researchers have identified numerous high-performance thermoelectric materials. For example, SnQ (Q= S, Se)^[13-16], Bi2Te3 alloy^[8, 11, 17, 18], PbQ (Q=S, Se, Te)^[19-22], Zintl phase^[23], Ag2Q (Q=S, Se, Te)^[24, 25], Mg₃X₂ (X=Sb, Bi)^[26, 27], half Heusler^[28], and most recently, the diamondoid compound^[29-32]. Early research on diamondoid compounds primarily concentrated on their optoelectronic properties, and their thermoelectric properties did not receive sufficient attention. Until the excellent thermoelectric properties of Cu2ZnSnSe4 and Cu₂CdSnSe₄ were first reported by Shi^[33] and Liu et al^[34]. in 2009, diamondoid thermoelectric materials have attracted widespread attention from the research community. Since then, a growing number of wide bandgap diamond -like materials have been reported, such as CuInTe2, CuGaTe2, CuFeS2, Cu2SnSe3, Cu3SbSe4, etc^{[30, 35-}] 41]. These materials derive from the sphalerite structure and has the typical tetrahedral coordination geometry of diamond. This stable twisted tetrahedral structure is formed by the "cross substitution" of element, following the "eight electron rule". Since the differences in electronegativity and radius between various anions and cations, phonon scattering in this twisted lattice is greatly enhanced, resulting in low κ . This characteristic is important for its decent thermoelectric performance. Quaternary Cu based diamondoid materials generally have a chemical formula of A ²BCQ ⁴, with a tetragonal lattice structure that exhibits a double -periodic cubic sphalerite structure along the z -direction, as shown in **Figure 1**. This complex crystal structure and elemental composition result in inherently low K . In addition, the diverse elemental

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composition provides it a broad scope to tune the band structure and electrical properties through chemical composition regulation. However, compared to the ternary diamondoid materials, the *ZT* value of A2BCQ⁴ compounds is lower, typically not exceeding 1.0, mainly due to their lower intrinsic σ . Therefore, a large amount of research aims to improve the electrical properties of quaternary diamondoid materials. Among these materials, Cu-based quaternary diamondoid materials have garnered the most attention. In the next, we start with introducing the recent progress in improving the electronic properties of these materials.

2 Optimization of Electrical Transport Performance

First, we start with introducing the recent
ties of these materials.
 FELECTTICAL Transport Performance

electrical properties is vital for promotion

functions of the material. However, the

S, these parameters are clo Improving the electrical properties is vital for promoting the thermoelectric performance of quaternary diamondoid materials. However, there is a strong coupling between their σ and *S*, these parameters are closely related to the carrier concentration ^{[22](#page-20-0)}/_{and} effective mass of the material. The σ is directly proportional to the carrier concentration and mobility:

$$
\sigma = e n \mu \tag{1}
$$

$$
n = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{\frac{3}{2}} F_{\frac{1}{2}}(\eta)
$$
 (2)

$$
\mu = \frac{2e}{3m^*} \tau_0 \left(\lambda + 1\right) \left(k_B T\right)^{\lambda - \frac{1}{2}} \frac{F_{\lambda}(\eta)}{F_{1/2}(\eta)}\tag{3}
$$

4 Among formulas, *n* is carrier concentration, μ is carrier mobility, \hat{m}^{\dagger} is effective mass of charge carrier, k_B is Boltzmann constant, *h* is planck constant, *n* is simplified Fermi level, τ_0 is relaxation time, λ is scattering factor. Based on the single parabolic band model and the relaxation time approximation, *S* can be derived from the following

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equation :

$$
S = \frac{8\pi^2 k_B^2 T}{3qh^2} m^* \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}
$$
(4)

From equations 1 to 4, we can see that optimizing carrier concentration by doping and adjusting [th](#page-18-0)e Fermi level can significantly enhance σ . Additionally, modifying the density of states by adjusting the band structure and effective mass plays a crucial role in improving the *S* .

2.1 Optimization of Carrier Concentration

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arrier concentration is one of the most dire
e. The carrier concentration in a material is i
ment doping is a common way to adjust the
rrow bandgap thermoelectrics ($E_g \le 0.5$ (
lectric materials Optimizing the carrier concentration is one of the most direct methods to enhance electrical performance. The carrier concentration in a material is influenced by its defect state s. Therefore, element doping is a common way to adjust the carrier concentration . Unlike traditional narrow bandgap thermoelectrics ($E_g \le 0.5$ eV), most of Cu-based diamondoid thermoelectric materials exhibit relatively wide bandgaps, *E*^g > 1eV, as shown in **Table1** . Because of the wide bandgap, most diamondoid materials have intrinsic low carrier concentrations, and element doping is a common and useful method to increase their carrier density and σ . modifying the
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Recently, many researchers have attempted various doping methods in quaternary diamondoid materials . According to the doping elements, they can be divided into intrinsic and extrinsic doping. Intrinsic doping or self-doping, occurs without introducing any other extrinsic elements, and achieve doping effect by regulating the stoichiometric ratio of the material. In Cu -based diamondoid materials, the predominant charge carriers responsible for electrical transport are holes . Given that

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s, but the insulating paths are also transfer
accement of Cd with Cu. As a result, the
ve value of 20300 S·m⁻¹⁸ at room temperatured at of the pristine sample. The same strate
ork in 2009^[42], where excess Cu was intr energy of copper vacancies is relatively small, these vacancies serve as intrinsic defects and significantly influencing the electrical properties of the material. In the early report by Liu et al in 2009 on Cu₂CdSnSe4^[34], substituting Cd with Cu can effectively improve the σ . They found the [Cu₂Se₄] tetrahedral slabs function as electrically conducting units, while the [SnCdSe4] units act as the electrically insulating structures. Thus, introducing excess Cu can not only introduce more intrinsic copper vacancies, generating more holes, but the insulating paths are also transformed into conductive ones due to the replacement of Cd with Cu. As a result, the σ of Cu_{2.1}Cd_{0.9}SnSe₄ achieved an impressive value of 20300 S·m⁻¹³ at room temperature, which is about six times higher than that of the pristine sample. The same strategy was successfully applied in another work in $2009^{[42]}$, where excess Cu was introduced into Cu₂ZnSnSe₄. This result in an impressive σ of 86000 S·m⁻¹ and achieved a groundbreaking ZT of 0.91 at 860K. Following these findings, many researchers adopted thi[s st](#page-20-0)rategy to improve the thermoelectric performance of diamondoid materials. For example, Qinghui Jiang et $al^{[43]}$ prepared Cu₂ZnSnS₄ samples using ball milling and hot press methods, and introduced additional Cu into the Zn sites to generate more hole carriers and improve σ . Finall[y, a](#page-18-0) high *ZT* value of 1.1 has been achieved for Cu_{2.125}Zn_{0.875}SnS₄. Besides, Yongkwan Dong et al^[44] explored introducing larger doses of Cu to further improve the σ of the material. Although introducing more low-valence cations at high valence sites has been proven to be an effective means of improving σ , excessive doping can easily lea[d to](#page-18-0) the formation of secondary phases. To address this, Zhou Li et al^[45] explored optimizing the carrier concentration by constructing different cation

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vacancies in Cu₂ZnSnSe₄, as shown in **Figure 2**. They studied the effects of three types of cationic vacancies, Cu, Zn, and Sn, on electrical properties, and found that all samples exhibited a significant increase in hole concentration compared to the pristine samples. Notably, the Sn-deficient sample achieved the highest carrier concentration of 7.5×10^{19} cm⁻³, resulting in an σ of 4700 S·m⁻¹.

mmonly used and effective optimization metric
ted to dope In at Sn site in Cu₂ZnSnSe₄, a
gnificantly improved the σ of the material
OK. Similarly, F. S. Liu et al^[46] explored th
e4 through experiment and theoret In addition to intrinsic doping, introducing extrinsic elements to increase the carrier concentration is a commonly used and effective optimization method. For example, X. Y. Shi et al^[33] attempted to dope In at Sn site in Cu₂ZnSnSe₄, achieving a high carrier concentration that significantly improved the σ of the material, resulting in a record high *ZT* of 0.95 at 850K. Similarly, F. S. Liu et al^[46] explored the role of doping Mn at Cd site in Cu₂CdSnSe₄ through experiment and theoretical calculation. They found that Mn doping causes the Fermi level to shift towards the valence band, resulting in a higher hole concentration while the carrier mobility decreases with increasing Mn content, ultimately leading to an increase in σ . Bo Wang et al^[47] also achieved a similar effect by doping Ga at the Sn site in Cu ²CdSnSe 4. T his strategy was also used in Cu₂CdSn_{0.9}In_{0.1}Se₄^[48], Cu₂MnSn_{0.95}In_{0.05}Se₄^[49] and Cu₂ZnSn_{0.95}Ga_{0.05}Se₄^[50], further demonstrating the effectiveness of extrinsic doping in enhancing the thermoelectric performance of quaternary diamondoid materials.

2.2 Optimization of Carrier Mobility

 $\frac{8}{11}$ is well known that, the carrier mobility of a material is closely related to the effective mass and scattering mechanism s. Therefore, a large amount of research on This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

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carrier mobility optimization has focused on these aspects. For example, Q. Song et $al^{[51]}$ optimized the lower intrinsic mobility of materials by manipulating th[e in](#page-18-0)trinsic lattice defects in Cu2FeSnSe4. They calculated the defect formation energies under both $\frac{2}{x}$ u-poor and [C](#page-18-0)u-rich conditions and identified the dominated defect types in Cu2FeSnSe4[. In](#page-19-0) the case of Cu deficiency (**Figure 3a**), the defect formation energy of 10 Cu vacancies is negative, indicating that Cu vacancies spontaneously occur during material preparation. Since the Cu vacancy is electronegative, making them to disrupt the original periodicity of the lattice $\frac{2}{x}$ ind introduce additional ionized impurity scattering centers, thus reducing the carrier mobility, as shown in **Figure 3c**.

Since the Cu vacancy is electronegative, noticely selectronegative, in
city of the lattice and introduce additions
as reducing the carrier mobility, as shown is
found that under $2u$ -rich condition, the defect
and the uni In contrast, they found that under $\frac{2}{x}$ u-rich condition, the defect formation energy [of C](#page-18-0)u atoms occupying Fe sites (Cu_{Fe} anti-site defect) is lower than that of Cu vacancies, indicating the Cu_{Fe} anti-site defect is dominant, as shown in **Figure 3b**. This defect is electrically neutral, so it causes only minimal disruption to the charge transport (**Figure 3d**). As a result, carrier mobility is less affected by scattering. Through carefully controlling the Cu content, they successfully achieved a synergistic optimization of both carrier mobility and carrier concentration. Furthermore, doping In into Cu₂MnSnSe₄ can also improve the carrier mobility of the material^[49]. This enhancement may be attributed to the optimization of band structure. In addition, by studying the transport properties of Cu2CoSnSe⁴ and Cu2CoSnS4. Taras Parashchuk et $a^{[52]}$ found that the selenide compound exhibited higher symmetry than its sulfide analogue, featuring with the bond angles closer to the ideal tetrahedral angle of 109.5°, this contribute to a higher carrier mobility.

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Improving the electrical transport properties by introducing a secondary phase is a novel method. For example, Sarita Devi Sharma et al^[53] improved the thermoelectric properties of C u 2 ZnSn S ⁴ by adding graphene nanosheets (GNs) into the matrix , as shown in **Figure 4**. The increase in σ_{1s}^{27} σ_{1s}^{27} σ_{1s}^{27} attributed to the formation of percolation channels created by the 2D graphene, which facilitates the transport of charge carriers. In this case, even small amount of GNs can produce a significant percolation effect . Additionally, the graphene nanosheets can exhibit a doping effect and moderately increases the carrier density of the material.

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In Ashfaq et al^[54] prepared a series of

the hydrothermal method, and found the

rematerial. This is because a small amount of

materix, forming bridge tha Similarly, Arslan Ashfaq et al^[54] prepared a series of Al-doped Cu₂ZnSnS₄ nanoparticles using the hydrothermal method, and found the extra Al effectively increases the σ of the material. This is because a small amount of Al particles diffuses into the gap of the matrix, forming bridge that allow charge carriers to pass freely through the grain boundaries, thus, increas e the carrier concentration and mobility simultaneously .

2.3 Optimization of Seebeck Coefficient

The *S* is closely related t[o th](#page-19-0)e density of states effective mass and carrier concentration. Although reducing carrier concentration is able to increase the *S*, it simultaneously lowers the σ . Therefore, band structure optimization emerges as a practical option to boost the S without compromising the σ . Cu-based quaternary diamondoid materials can exhibit two distinct crystal structures, the highly ordered Stannite and the disordered Kesterite . The symmetry of these crystal structure s directly impacts the band structure of materials . Various methods have been developed to

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with the disordered structure. At the same drops at the phase transition temperature, and drops at the phase transition temperature, are in the only the first three valence bands decrease, be band gap also decreases, as s optimize the band structure and transport properties through manipulating the crystal structure. Eleonora Isotta et al^[55] demonstrated that the transition from an ordered to a disordered structure in Cu2ZnSnS⁴ improves the thermoelectric properties of materials, primarily due to alterations in the electronic band structure as shown in **Figure 5**. They found a second-order reversible phase transition occurring near 533K. **Figure 5a** shows that the *S* increases sharply around the transition temperature, attributed to the higher symmetry associated with the disordered structure. At the same time, the σ of the material dramatically drops at the phase transition temperature, as shown in **Figure 5b**. Through the electronic band calculation, they found that in disordered structure[s, th](#page-18-0)e energy difference among the first three valence bands decreas[e, th](#page-18-0)e top of the valence band flattens, and the band gap also decreases, as shown in the **Figure 5c**. Following this, Akira Nagaoka et al^[56] employed a pseudo-cubic strategy [to](#page-18-0) enhance the thermoelectric performance of Cu2ZnSnS⁴ single crystal, as shown in **Figure 6**. They obtained the degenerate electron energy bands in the pseudo-cubic structure, resulting in a high *S* and a remarkable *ZT* value of 1.6 at 800K in the material.

In addition, several methods can effectively improve the *S* of materials without altering their band structure. For example, by introducing energy barriers at the interface through doping or incorporation of secondary phase, low-energy carriers would be greatly scattered while high-energy carriers can pass through, achieving the goal of improving *S*. Qiufan Chen et al^[57] doped Ag atoms into Cu₂CdSnSe₄ using a chemical method, successfully embedding a disordered sphalerite structure within the ordered sphalerite phase. This modification caused the energy band at the interface to

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bend, thereby generating energy barriers that effectively scatter low -energy carriers. As a result, both the *S* and σ were improved. Jolly Jacob et al^[58] adopted a similar strategy by doping Cd into C u 2 ZnSn S ⁴ and found that the *S* increased with adding Cd. They found that, I doping led to the formation of Cu[-ba](#page-18-0)sed secondary phases. These secondary phases serve as effective filters for low-energy carriers, while allowing only high -energy carriers to pass through, thereby improving the performance of material . Additionally, introducing spin entropy by doping magnetic particles such as $Ni^[59]$ or elements such as Pb and Te^[60] can effectively increase the effective mass and improve the *S* of the material.

3 Optimization of Thermal Transport Performance

cing spin entropy by doping magnetic par
and Te^[60] can effectively increase the effectively
increase the effectively increase the effectively
free effectively increase the effectively increase the transfer of thermal e We know that the transfer of thermal energy is mainly achieved through lattice vibrations and carrier transport, with the former represented as [la](#page-19-0)ttice thermal conductivity κ_1 and the latter as electronic thermal conductivity $\kappa_{\rm e}$. They can be represented as:

$$
\kappa_l = \frac{1}{3} C_V \nu l \tag{5}
$$

$$
\kappa_e = L\sigma T\tag{6}
$$

In the above equation, C_v i[s sp](#page-18-0)ecific heat at constant volume of materials, v is phonon velocity, l is mean free path of phonon collision^[61], L is Lorentz constant. Although the complex crystal structure and elemental composition of Cu -based quaternary diamondoid materials result in relatively low intrinsic thermal conductivity, there is still room for further optimization. Unlike κ _e, κ is almost independent of other electronic transport parameters, and can be regulated independently. To this end, many researchers have focused on reducing the κ to improve the thermoelectric performance. Defect control and microstructure design are two effective methods for reducing κ .

3.1 Defect Control

e material. So far, introducing appropriate
mained the main strategy for suppressing *i*
the fluctuation of the mass rield caused by d
f the stress field caused by different atomi
er the scattering effect on high-frequenc Compared to C_v and v , the *l* is easier to regulate, particularly through controlling the defects state in the material. So far, introducing appropriate defects into the lattice to reduce the l has remained the main strategy for suppressing κ . The impact of point defects mainly lies in the fluctuation of the mass field caused by different atomic masses and the fluctuation of the stress field caused by different atomic radii. The larger the difference, the stronger the scattering effect on high-frequency phonons, and the better the result in reducing κ . For example, Qiufan Chen et al^[57] prepared Ag-doped Cu₂CdSnSe₄ using a chemical method, which introduced Ag_{Cu} point defects into the matrix, distorting the crystal structure and enhancing the phonon scattering. In addition, O ingfeng Song et al^[62] introduced excess Cu into Cu₂MnSnSe₄, increasing local lattice distortion and suppressing κ . Studies also indicate that replacing Zn with Co in Cu2ZnSnSe⁴ increases point defects, reduces phonon relaxation time, and thus decrease κ_1 [63]. Besides, anionic substitution significantly reduces the κ_1 of Cu₂ZnGeSe_{4-x}S_x^[64], primarily due to the disorder caused by substitution. Ultra-low κ can also be achieved in the locally disordered $Cu_{2+x}Zn_{1-x}SnS4^{[43]}$, which is mainly attributed to the highly disordered arrangement of Cu and Zn in the lattice, causing phonon localization and shortening the phonon mean free path. Some researchers also use lattice strain to

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regulate the thermoelectric properties of materials^[65]. They introduce lattice strain by creating dislocations, which reduc e the relaxation time of phonons and enhanc e their scattering , as shown in **Figure 7** .

3.2 Microstructure Design

Jia Fan et al^[66] synthesized Cu₂CdSnSe₄
nd prepared bulk materials by hot pressinted more grain boundaries, significantl
ted more grain boundaries, significantl
ately resulted in a thermal conductivity of
s about 40 13 In addition to introducing point defects, microstructure design, such as nano precipitate, nanocrystalline material, and secondary phase boundary, can also reduce κ . For example, Feng-Jia Fan et al^[66] synthesized Cu₂CdSnSe4 nanocrystals through colloidal synthesis and prepared bulk materials by hot pressing. In their work, the nanocrystal s generated more grain boundaries, significantly enhancing phonon scattering. This ultimately resulted in a thermal conductivity of 1.7 W m⁻¹ K⁻¹at room temperature, which is about 40% lower than that of the bulk sample prepared by solid state reaction. After that, Kaya Wei et al $[67]$ reported the preparation of nanostructured Cu₂ZnSnSe4 and Ag₂ZnSnSe4, once again confirming the impact of nanomaterials on the κ of these materials. Combining bulk materials with nanocrystals can reduce $\frac{26}{10}$ $\frac{26}{10}$ $\frac{26}{10}$ ermal conductivity while maintaining the high electrical properties of the bulk material. Qiufan Chen et al^[68] prepared Cu₂CdSnSe4 nanocrystals suing colloidal synthesis and added these nanocrystals into the C u 2 CdSn S e ⁴ matrix , as shown in **Figure 8**. They found that this hierarchical architecture is able to suppress the thermal conductivity while preserve the decent electrical properties . The increased grain boundaries and embedded nanocrystals significantly enhanced phonon scattering, especially the latter serving as an additional scattering center that effectively scatter medium to long wavelength phonons, thereby reducing κ . Himanshu Nautiyal et al^[69]

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synthesized disordered nanostructured polycrystals of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ through high-energy reaction mechanical alloying, achieving $\frac{15}{d}$ low thermal conductivity of $0.2 \text{ W m}^{-1} \text{ K}^{-1}$. Similar studies have also been conducted by Binayak Mukherjee et al^[70], who obtained cubic Cu₂ZnSnSe₄ nanostructures with [a lo](#page-18-0)w thermal conductivity of $0.21W \text{ m}^{-1} \text{ K}^{-1}$.

For th[e](#page-18-0)rmal conductivity through the introversies

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hu et al^[71] replaced Sn with Pb in Cu₂ZnSn

he PbSe framework, distributed as a se The optimization of thermal conductivity through the introduction of secondary phase grain boundary engineering has also been proven to be an effective method. The interface between the secondary phase and the matrix generates strong phonon scattering. Yingcai Zhu et al^[71] replaced Sn with Pb in $Cu₂ZnSnSe₄$ and found that Pb primarily exists in the PbSe framework, distributed as a secondary phase at grain boundaries, as shown in **Figure 9**. The phase interface between the secondary phase and the matrix has a strong scattering effect on phonons. Additionally, the smaller grain [si](#page-18-0)ze of the secondary phase increases the density of grain boundaries and further reduces the κ . Furthermore, the composite of CdSe and Cu₂CdSnSe₄ forms a coherent phase interface, allowing charge carriers to pass through while scattering phonons across a wide frequency spectrum^[72]. The Cd vaporization during the hot pressing, creating nanopores in the material that introduce additional scattering centers, significantly reducing the κ .

4 Summary and Outlook

14 Recently, diamondoid thermoelectric materials have gained significant attention due to their unique electronic and thermal transport properties. Although their

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ing pathways for future optimization. If

has been thermoelectric performance has yet to reach the levels of traditional thermoelectric materials, they are still a new star with great research potential. This article focuses on Cu -based quaternary diamondoid materials and provides a collection of recent progress and a comprehensive view of the optimization strategies for improving their electrical and thermal properties. We have thoroughly discussed the influence of various defects on [th](#page-18-0)e carrier concentration, carrier mobility and the band structure of the Cu-based quaternary diamondoid materials . Additionally, we have summarize d a series of effective methods to enhance the phonon scattering and suppress the thermal conductivity. Overall, improving the carrier mobility while further reducing the thermal conductivity is critical for achieving high thermoelectric performance in these materials. In this context, the recently proposed off-centering effect may offer a new perspective and provide promising pathways for future optimization . In summary, although significant progress has been made in promoting the thermoelectric performance of these system s, many challenges remain unresolved . We hope this review provide fresh insights and sparks new ideas for further improving the thermoelectric performance of these promising material s .

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Dear Editor,

Please find our revised paper **MATLAB-2024-0005** titled "**Recent Progress on Quaternary Copper-based Diamondoid Thermoelectric Materials**". We appreciate the careful examination of our paper by the referees and are grateful for their comments and constructive criticism.

We have revised our paper (**modifications are highlighted in yellow**) and provided a point-by-point response and description of the revisions.

Description of the revisions:

1. The accurate use of symbols has been corrected and added to page 2, page 22 and pages 27 - 29 in the revised manuscript. (Reviewer #1, Comment #1)

evised manuscript. (Reviewer #1, Comment expressions in the manuscript have been
ges 13 -14 in the revised manuscript. (Reviewer #2, Commet #4, Comment #5; Reviewer #2, Commet account Ferre 2, Commet #2)
reviewer #2, Comme 2. The relevant grammar expressions in the manuscript have been modified and added to pages 3 - 9 and pages 13 -14 in the revised manuscript. (Reviewer #1, Comment #2, Comment #3, Comment #4, Comment #5; Reviewer #2, Comment #4)

3. The discussion section regarding Figs. 3e and 3f has been added to page 8 in the revised manuscript. (Reviewer #2, Comment #2)

We trust that with the changes made to text and figure, the paper is now suitable for publication in *Materials Lab* .

Thank you again and we are looking forward to hearing from you.

Best regards. Hongyao Xie

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Reviewer(s)' Comments to Author: **Reviewer: 1**

This paper summarized the recent progress on diamondoid $Cu₂ZnSnSe₄$ thermoelectric materials, introduced a series of optimization strategies and outlined the current challenges faced by the material. I think this work provide some new ideas for further improving the performance of $Cu₂ZnSnSe₄$ system. I recommend this work to be published after some minor revisions. My detailed comment and suggestions are listed below.

Question/Comments 1: The authors mentioned that 'total thermal conductivity of the material k tol'. Please correct it to 'total thermal conductivity of the material k tot'. See page 2 and elsewhere in the text.

Reply: Thank you for the reminder. The symbol of total thermal conductivity was revised.

Question/Comments 2: The authors mentioned that 'in 2009, diamondoid thermoelectric materials have attracted widespread attention from the research community'. Please correct it to 'In 2009, diamondoid thermoelectric materials have attracted widespread attention from the research community'. See page 3.

Reply: Thank you for the reminder. The corresponding statement was corrected.

Question/Comments 3: The authors mentioned 'carrier density', please change it to 'carrier concentrations' See page 5.

Reply: Thanks for the suggestion, we carefully revised this issue and paid attention to the consistency of the wording in the manuscript.

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rials have attracted widespread attentio
correct it to 'In 2009, diamondoid thermod
attention from the research community'. Se
for the reminder. The corresponding statem
to 15 3: T *Question/Comments 4:* The authors mentioned 'Given that the formation energy of copper vacancies is relatively small, these vacancies serve as intrinsic defects and significantly influencing the electrical properties of the material', please change it to 'Given that the formation energy of copper vacancies is relatively small, these vacancies serve as intrinsic defects significantly influencing the electrical properties of the material'. See page 6.

Reply: Thanks for the suggestion. The corresponding statement was corrected.

Question/Comments 5: The authors mentioned 'Additionally, the graphene nanosheets can exhibit a doping effect and moderately increases the carrier density of the material'. Please change 'increases' to 'increase'. See page 9.

Reply: Thanks for the suggestion. This issue was revised.

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Reviewer: 2

In this paper, the authors discuss quaternary copper-based diamondoid materials for thermoelectric applications. The paper reviews progress in improving their electrical transport properties and reducing thermal conductivity while identifying current research challenges and suggesting future directions. This review is important because copper-based diamondoid materials offer advantages such as elemental abundance, low toxicity, and unique transport characteristics. The paper is well-written and includes all the key milestones in the development of copper-based diamondoid materials, making it a valuable reference for future studies. I recommend accepting this paper for publication after addressing the following issues.

Question/Comments 1: On Page 8, the authors mention that CuFe is an electrically neutral anti-site defect. However, in Fig. 3e, the carrier concentration nearly doubles in Cu2+xFe1-xSnSe4 when x changes from 0 to 0.1. What could be the potential reason for this systematic change in carrier concentration?

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the suggestion. The statement of "CuFe is e
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be misleading. In reality, when Cu is dope
with a small fraction exhibiting +1 oxidation
on slightly in *Reply:* Thanks for the suggestion. The statement of "CuFe is electrically neutral antisite defect" is referenced from the corresponding literature. and we recognize that this characterization may be misleading. In reality, when Cu is doped into Fe site, most of the Cu behave as $+2$, with a small fraction exhibiting $+1$ oxidation state. Consequently, the hole concentration slightly increases with adding Cu. But the increment is very minimal, indicating that the CuFe anti-site defect is nearly electrically neutral. We have corrected the corresponding statement to reflect this understanding.

Question/Comments 2: In the manuscript, Figs. 3e and 3f are present but not discussed in the text. I recommend that the authors either remove these figures or add a relevant discussion if they are important.

Reply: Thanks for the suggestion. We added a relevant discussion on page 8 for Figs. 3e and 3f in order to demonstrate the effectiveness of this regulatory strategy in improving the electrical properties of materials.

Question/Comments 3: On page 9, the authors state that adding graphene nanosheets to Cu2ZnSnS4 significantly improves electrical conductivity. Does this result in anisotropic transport properties in the composite, as graphene sheets can become highly oriented after hot pressing?

Reply: Thanks for the suggestion. Some layer materials, such as BiCuSeO, introducing the graphene can enhance their orientation and results in anisotropic transport properties. In contrast, diamondoid compounds have a pseudo-cubic structure and exhibit weak anisotropy. Adding graphene to Cu2ZnSnS4 does not improve the preferred orientation of the matrix. Moreover, the SEM images reveal that the distribution of graphenes within Cu2ZnSnS4 is uniform and their orientation is random. Therefore, while the hot pressing of graphene into Cu2ZnSnS4 may induce some degree of anisotropic, it is unlikely to be significant.

Question/Comments 4: There are a few minor grammatical issues that need to be addressed. On page 14, it should be 'using' instead of 'suing,' 'preserving' instead of

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'preserve,' 'additional scattering centers' instead of 'an additional scattering center,' and 'the introduction of secondary phase grain boundary engineering' is an awkward expression. Is this correct? Should it be 'grain boundary engineering through the introduction of a secondary phase'?

Reply: Thanks for the suggestion. We greatly appreciate you pointing out these grammar issues. We have double checked the manuscript and corrected all mistakes.

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Recent Progress on Quaternary Copper-based Diamondoid Thermoelectric Materials

Zihao Zhao¹, Hongyao Xie^{1,*}, Li-Dong Zhao^{1,*}

¹*School of Materials Science and Engineering, Beihang University, Beijing 100191, China.*

E-mail: xiehongyao@buaa.edu.cn; *zhaolidong@buaa.edu.cn*

g sustainable new energy and high-efficion-
belectric technology has gained attention of
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c elemental composition. Recently, qua
s have garnere **Abstract**: The rising concern on energy and environmental crises have sparked global interest in developing sustainable new energy and high-efficient energy conversion technologies. Thermoelectric technology has gained attention due to its potential for application in waste heat recovery and solid-state refrigeration. However, the application of traditional thermoelectric materials remains limited due to their expensive and toxic elemental composition. Recently, quaternary copper-based diamondoid materials have garnered significant interest due to their unique transport properties, high element abundance, and low toxicity. Many of these materials have demonstrated promising *ZT* value, positioning them as potential candidates for efficient thermoelectric applications. This paper summarizes the recent progress in copper-based quaternary diamondoid materials. We present a collection of research focused on optimizing electrical transport properties through carrier concentration tuning and band engineering, along with an overview of reducing thermal conductivity *via* microstructure enhanced phonon scattering. Finally, we analyze the current research bottlenecks in copper-based quaternary diamondoid thermoelectric materials and propose future research directions.

Keywords : quaternary Cu-based diamondoid materials, thermoelectric performance, carrier concentration, band engineering, microstructure

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1 Introduction

columns. Intermoductive materials¹²⁻⁴, based
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ons^[6].
Figure of the moductive materials is moductive figure of merit The continuous rise in global energy demand and the depletion of unrenewable fossil fuels have made the development of sustainable new energy and high-efficiency energy conversion technologies become the worldwide topics. Research indicates that approximately 65% of energy produced in human activities is wasted and lost as heat^[1]. Thus, developing effective methods to recovery this waste heat is considered as a way to solve the energy problems. Thermoelectric materials $[2-4]$, based on the Seebeck effect, can directly convert heat into electricity, and can also be used for solid state cooling. This makes them a promising tool for mitigating energy crises[5]. However, the low energy conversion efficiency of thermoelectric materials limits their large-scale commercial applications^[6]. wide topics. Research indicates that
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Generally, the performance of thermoelectric materials is mainly evaluated by the dimensionless thermoelectric figure of merit ZT, $ZT = S^2 \sigma T / \kappa_{tot} = S^2 \sigma T / (\kappa_{e} + \kappa_{l}),$ where *S* is Seebeck coefficient, σ is electrical conductivity, *T* is absolute temperature, κ_{e} is electronic thermal conductivity, κ_{1} is lattice thermal conductivity, and the sum of κ _c and κ _l is the total thermal conductivity of the material $\kappa_{\text{tot}}^{[7-9]}$ d on the Seebeck effect,
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 $PF = S^2 \sigma$, which is
 a power factor used to characterize the electrical transport performance of thermoelectric materials. Therefore, to improve the performance of thermoelectric materials, two main approaches are typically pursued: (1) optimizing the electrical properties; (2) reducing thermal conductivity^[10, 11]. However, because of the strong inherent coupling between electrical conductivity σ , Seebeck coefficient *S*, and thermal conductivity κ_{tot} , it is challenging to solely regulate these parameters to achieve high

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thermoelectric performance^[12]. For instance, increasing the carrier concentration can enhance σ , but this often reduces the S and increases κ _e, limiting the overall improvement in *ZT*. To overcome this, researchers employ various strategies to decouple these properties, aiming for enhanced thermoelectric efficiency.

 $[Q=8, Se, Ie)^{[1/2+2]}$, Zinti phase^[25], Ag₂Q_{26, 27]}, half Heusler^[28], and most rece y research on diamondoid compounds principroperties, and their thermoelectric properties for properties, and their thermoelectric Since the discovery of thermoelectric effect, researchers have identified numerous high-performance thermoelectric materials. For example, SnQ ($Q = S$, Se)^[13-16], Bi₂Te₃ alloy^[8, 11, 17, 18], PbQ (Q=S, Se, Te)^[19-22], Zintl phase^[23], Ag₂Q (Q=S, Se, Te)^[24, 25], Mg_3X_2 (X=Sb, Bi)^[26, 27], half Heusler^[28], and most recently, the diamondoid compound[29-32]. Early research on diamondoid compounds primarily concentrated on their optoelectronic properties, and their thermoelectric properties did not receive sufficient attention. Until the excellent thermoelectric properties of Cu₂ZnSnSe₄ and $Cu₂CdSnSe₄$ were first reported by Shi^[33] and Liu et al^[34]. In 2009, diamondoid thermoelectric materials have attracted widespread attention from the research community. Since then, a growing number of wide bandgap diamond-like materials have been reported, such as CuInTe₂, CuGaTe₂, CuFeS₂, Cu₂SnSe₃, Cu₃SbSe₄, etc^{[30,} ³⁵⁻⁴¹. These materials derive from the sphalerite structure and has the typical tetrahedral coordination geometry of diamond. This stable twisted tetrahedral structure is formed by the "cross substitution" of element, following the "eight electron rule". Since the differences in electronegativity and radius between various anions and cations, phonon scattering in this twisted lattice is greatly enhanced, resulting in low κ . This characteristic is important for its decent thermoelectric performance. Quaternary Cubased diamondoid materials generally have a chemical formula of A_2BCQ_4 , with a

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F Ele tetragonal lattice structure that exhibits a double-periodic cubic sphalerite structure along the z-direction, as shown in **Figure 1**. This complex crystal structure and elemental composition result in inherently low κ . In addition, the diverse elemental composition provides it a broad scope to tune the band structure and electrical properties through chemical composition regulation. However, compared to the ternary diamondoid materials, the ZT value of A_2BCQ_4 compounds is lower, typically not exceeding 1.0, mainly due to their lower intrinsic σ . Therefore, a large amount of research aims to improve the electrical properties of quaternary diamondoid materials. Among these materials, Cu-based quaternary diamondoid materials have garnered the most attention. In the next, we start with introducing the recent progress in improving the electronic properties of these materials.

2 Optimization of Electrical Transport Performance

Improving the electrical properties is vital for promoting the thermoelectric performance of quaternary diamondoid materials. However, there is a strong coupling between their σ and *S*, these parameters are closely related to the carrier concentration and effective mass of the material. The σ is directly proportional to the carrier concentration and mobility: *s*
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n = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{\frac{3}{2}} F_{\frac{1}{2}}(\eta)
$$
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\mu = \frac{2e}{3m^*} \tau_0 \left(\lambda + 1\right) \left(k_B T\right)^{\lambda - \frac{1}{2}} \frac{F_\lambda(\eta)}{F_{1/2}(\eta)}\tag{3}
$$

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Among formulas, *n* is carrier concentration, μ is carrier mobility, m^* is effective mass of charge carrier, k_B is Boltzmann constant, h is planck constant, η is simplified Fermi level, τ_0 is relaxation time, λ is scattering factor. Based on the single parabolic band model and the relaxation time approximation, *S* can be derived from the following equation: ntration, μ is carrier mobility, m^* is effective mass
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tering factor. Based on the single parabolic band
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necentration, μ is carrier mobility, m^* is effective mass

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$$
S = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}
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4, we can see that optimizing carrier concerned
level can significantly enhance σ . Addition
djusting the band structure and effective material
djusting the band structure and effective material
of **Carrier Concentratio** From equations 1 to 4, we can see that optimizing carrier concentration by doping and adjusting the Fermi level can significantly enhance σ . Additionally, modifying the density of states by adjusting the band structure and effective mass plays a crucial role in improving the *S* .

2.1 Optimization of Carrier Concentration

Optimizing the carrier concentration is one of the most direct methods to enhance electrical performance. The carrier concentration in a material is influenced by its defect states. Therefore, element doping is a common way to adjust the carrier concentration. Unlike traditional narrow bandgap thermoelectrics ($E_g \le 0.5$ eV), most of Cu-based diamondoid thermoelectric materials exhibit relatively wide bandgaps, E_g > 1eV, as shown in **Table1**. Because of the wide bandgap, most diamondoid materials have intrinsic low carrier concentrations, and element doping is a common and useful method to increase their carrier concentrations and σ .

Recently, many researchers have attempted various doping methods in quaternary

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ing the electrical properties of the material
Cu₂CdSnSe₄^[34], substituting Cd with Cu ca
ne [Cu₂Se₄] tetrahedral slabs function as ϵ
CdSe₄] units act as the electrically insulate
Cu can not only introduce m diamondoid materials. According to the doping elements, they can be divided into intrinsic and extrinsic doping. Intrinsic doping or self-doping, occurs without introducing any other extrinsic elements, and achieve doping effect by regulating the stoichiometric ratio of the material. In Cu-based diamondoid materials, the predominant charge carriers responsible for electrical transport are holes. Given that the formation energy of copper vacancies is relatively small, these vacancies serve as intrinsic defects significantly influencing the electrical properties of the material. In the early report by Liu et al in 2009 on $Cu_2CdSnSe_4^{[34]}$, substituting Cd with Cu can effectively improve the σ . They found the $\lceil Cu_2Se_4 \rceil$ tetrahedral slabs function as electrically conducting units, while the $[SnCdSe_4]$ units act as the electrically insulating structures. Thus, introducing excess Cu can not only introduce more intrinsic copper vacancies, generating more holes, but the insulating paths are also transformed into conductive ones due to the replacement of Cd with Cu. As a result, the σ of Cu_{2.1}Cd_{0.9}SnSe₄ achieved an impressive value of 20300 S·m-1 at room temperature, which is about six times higher than that of the pristine sample. The same strategy was successfully applied in another work in 2009^[42], where excess Cu was introduced into $Cu₂ZnSnSe₄$. This result in an impressive σ of 86000 S·m⁻¹ and achieved a groundbreaking *ZT* of 0.91 at 860K. Following these findings, many researchers adopted this strategy to improve the thermoelectric performance of diamondoid materials. For example, Qinghui Jiang et al^[43] prepared $Cu₂ZnSnS₄$ samples using ball milling and hot press methods, and introduced additional Cu into the Zn sites to generate more hole carriers and improve σ . Finally, a high *ZT* value of 1.1 has been achieved for Cu_{2.125}Zn_{0.875}SnS₄.

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Besides, Yongkwan Dong et al^[44] explored introducing larger doses of Cu to further improve the σ of the material. Although introducing more low-valence cations at high valence sites has been proven to be an effective means of improving σ , excessive doping can easily lead to the formation of secondary phases. To address this, Zhou Li et al[45] explored optimizing the carrier concentration by constructing different cation vacancies in Cu ²ZnSnSe ⁴, as shown in **Figure 2**. They studied the effects of three types of cationic vacancies, Cu, Zn, and Sn, on electrical properties, and found that all samples exhibited a significant increase in hole concentration compared to the pristine samples. Notably, the Sn-deficient sample achieved the highest carrier concentration of 7.5 \times 10¹⁹ cm⁻³, resulting in an σ of 4700 S·m⁻¹.

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ignificant increase in hole concentration contents.
The Sn-deficient sample achieved the highest comparent and σ of 4700 S·m⁻¹.
Trinsic doping, introducing extrinsic elem In addition to intrinsic doping, introducing extrinsic elements to increase the carrier concentration is a commonly used and effective optimization method. For example, X. Y. Shi et al^[33] attempted to dope In at Sn site in $Cu₂ZnSnSe₄$, achieving a high carrier concentration that significantly improved the σ of the material, resulting in a record high *ZT* of 0.95 at 850K. Similarly, F. S. Liu et al^[46] explored the role of doping Mn at Cd site in Cu ²CdSnSe ⁴ through experiment and theoretical calculation. They found that Mn doping causes the Fermi level to shift towards the valence band, resulting in a higher hole concentration while the carrier mobility decreases with increasing Mn content, ultimately leading to an increase in σ . Bo Wang et al^[47] also achieved a similar effect by doping Ga at the Sn site in Cu ²CdSnSe ⁴. This strategy was also used in $Cu_2CdSn_{0.9}In_{0.1}Se_4^{[48]}$, $Cu_2MnSn_{0.95}In_{0.05}Se_4^{[49]}$ and $Cu_2ZnSn_{0.95}Ga_{0.05}Se_4^{[50]}$, further demonstrating the effectiveness of extrinsic doping in enhancing the thermoelectric This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

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performance of quaternary diamondoid materials.

2.2 Optimization of Carrier Mobility

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the conditions and identified the domination
ase of Cu deficiency (**Figure 3a**), the defective, indicating that Cu vacancies It is well known that, the carrier mobility of a material is closely related to the effective mass and scattering mechanisms. Therefore, a large amount of research on carrier mobility optimization has focused on these aspects. For example, Q. Song et $al^{[51]}$ optimized the lower intrinsic mobility of materials by manipulating the intrinsic lattice defects in $Cu₂FeSnSe₄$. They calculated the defect formation energies under both Cu-poor and Cu-rich conditions and identified the dominated defect types in Cu2FeSnSe4. In the case of Cu deficiency (**Figure 3a**), the defect formation energy of Cu vacancies is negative, indicating that Cu vacancies spontaneously occur during material preparation. Since the Cu vacancy is electronegative, making them to disrupt the original periodicity of the lattice and introduce additional ionized impurity scattering centers, thus reducing the carrier mobility, as shown in **Figure 3c**.

In contrast, they found that under Cu-rich condition, the defect formation energy of Cu atoms occupying Fe sites (Cu_{Fe} anti-site defect) is lower than that of Cu vacancies, indicating the Cu_{Fe} anti-site defect is dominant, as shown in **Figure 3b**. This defect is almost electrically neutral, so it causes only minimal disruption to the charge transport (**Figure 3d**). As a result, carrier mobility is less affected by scattering. Through carefully controlling the Cu content, they successfully achieved a synergistic optimization of both carrier mobility and carrier concentration, as shown in **Figure 3e**. And ultimately, it increased the conductivity of the material by about 2.5 times, as

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shown in Figure 3f. Furthermore, doping In into Cu₂MnSnSe₄ can also improve the carrier mobility of the material^[49]. This enhancement may be attributed to the optimization of band structure. In addition, by studying the transport properties of $Cu₂CoSnSe₄$ and $Cu₂CoSnS₄$. Taras Parashchuk et al^[52] found that the selenide compound exhibited higher symmetry than its sulfide analogue, featuring with the bond angles closer to the ideal tetrahedral angle of 109.5°, this contribute to a higher carrier mobility.

ectrical transport properties by introducing
sample, Sarita Devi Sharma et al^[53] impro
SnS₄ by adding graphene nanosheets (GN
The increase in σ is attributed to the for
he 2D graphene, which facilitates the transp Improving the electrical transport properties by introducing a secondary phase is a novel method. For example, Sarita Devi Sharma et al^[53] improved the thermoelectric properties of Cu ²ZnSnS ⁴ by adding graphene nanosheets (GNs) into the matrix, as shown in **Figure 4**. The increase in σ is attributed to the formation of percolation channels created by the 2D graphene, which facilitates the transport of charge carriers. In this case, even small amount of GNs can produce a significant percolation effect. Additionally, the graphene nanosheets can exhibit a doping effect and moderately increase the carrier concentrations of the material.

Similarly, Arslan Ashfaq et al^[54] prepared a series of Al-doped Cu₂ZnSnS₄ nanoparticles using the hydrothermal method, and found the extra Al effectively increases the σ of the material. This is because a small amount of Al particles diffuses into the gap of the matrix, forming bridge that allow charge carriers to pass freely through the grain boundaries, thus, increase the carrier concentration and mobility simultaneously.

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2.3 Optimization of Seebeck Coefficient

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sotta et al^[55] demonstrated that the transition
n Cu₂ZnSnS₄ improves the thermoelectr The *S* is closely related to the density of states effective mass and carrier concentration. Although reducing carrier concentration is able to increase the *S*, it simultaneously lowers the σ . Therefore, band structure optimization emerges as a practical option to boost the *S* without compromising the σ . Cu-based quaternary diamondoid materials can exhibit two distinct crystal structures, the highly ordered Stannite and the disordered Kesterite. The symmetry of these crystal structures directly impacts the band structure of materials. Various methods have been developed to optimize the band structure and transport properties through manipulating the crystal structure. Eleonora Isotta et al^[55] demonstrated that the transition from an ordered to a disordered structure in $Cu₂ZnSnS₄$ improves the thermoelectric properties of materials, primarily due to alterations in the electronic band structure as shown in **Figure 5**. They found a second-order reversible phase transition occurring near 533K. **Figure 5a** shows that the *S* increases sharply around the transition temperature, attributed to the higher symmetry associated with the disordered structure. At the same time, the σ of the material dramatically drops at the phase transition temperature, as shown in **Figure 5b**. Through the electronic band calculation, they found that in disordered structures, the energy difference among the first three valence bands decrease, the top of the valence band flattens, and the band gap also decreases, as shown in the **Figure 5c**. Following this, Akira Nagaoka et al^[56] employed a pseudo-cubic strategy to enhance the thermoelectric performance of Cu₂ZnSnS₄ single crystal, as shown in **Figure 6**. They obtained the degenerate electron energy bands in the pseudo-cubic structure, resulting

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in a high *S* and a remarkable *ZT* value of 1.6 at 800K in the material.

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of σ were improved. Jolly Jacob et al^[58] add
u₂ZnSnS₄ and found that the *S* In addition, several methods can effectively improve the *S* of materials without altering their band structure. For example, by introducing energy barriers at the interface through doping or incorporation of secondary phase, low-energy carriers would be greatly scattered while high-energy carriers can pass through, achieving the goal of improving S. Qiufan Chen et al^[57] doped Ag atoms into Cu₂CdSnSe₄ using a chemical method, successfully embedding a disordered sphalerite structure within the ordered sphalerite phase. This modification caused the energy band at the interface to bend, thereby generating energy barriers that effectively scatter low-energy carriers. As a result, both the *S* and σ were improved. Jolly Jacob et al^[58] adopted a similar strategy by doping Cd into Cu ²ZnSnS ⁴ and found that the *S* increased with adding Cd. They found that, Cd doping led to the formation of Cu-based secondary phases. These secondary phases serve as effective filters for low-energy carriers, while allowing only high-energy carriers to pass through, thereby improving the performance of material. Additionally, introducing spin entropy by doping magnetic particles such as Ni^[59] or elements such as Pb and Te^[60] can effectively increase the effective mass and improve the *S* of the material.

3 Optimization of Thermal Transport Performance

We know that the transfer of thermal energy is mainly achieved through lattice vibrations and carrier transport, with the former represented as lattice thermal conductivity κ_1 and the latter as electronic thermal conductivity κ_e . They can be
represented as:

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eat at constant volume of materials, *v* is phonon collision^[61], *L* is Lorentz constant. Although the} In the above equation, C_v is specific heat at constant volume of materials, v is phonon velocity, l is mean free path of phonon collision^[61], L is Lorentz constant. Although the complex crystal structure and elemental composition of Cu-based quaternary diamondoid materials result in relatively low intrinsic thermal conductivity, there is still room for further optimization. Unlike κ _e, κ _l is almost independent of other electronic transport parameters, and can be regulated independently. To this end, many researchers have focused on reducing the κ_1 to improve the thermoelectric performance. Defect control and microstructure design are two effective methods for reducing κ .

3.1 Defect Control

Compared to C_v and v , the *l* is easier to regulate, particularly through controlling the defects state in the material. So far, introducing appropriate defects into the lattice to reduce the l has remained the main strategy for suppressing κ_l . The impact of point defects mainly lies in the fluctuation of the mass field caused by different atomic masses and the fluctuation of the stress field caused by different atomic radii. The larger the difference, the stronger the scattering effect on high-frequency phonons, and the better the result in reducing κ . For example, Qiufan Chen et al^[57] prepared Ag-doped $Cu₂CdSnSe₄$ using a chemical method, which introduced Ag_{Cu} point defects into the

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Fred Cu_{2+x}Zn_{1-x}SnS₄⁺⁺²¹, which is mainly a
ent of Cu and Zn in the lattice, causing ph
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lectric properties of materials^[65]. They intr
which reduce the relaxation time of p matrix, distorting the crystal structure and enhancing the phonon scattering. In addition, Qingfeng Song et al^[62] introduced excess Cu into $Cu₂MnSnSe₄$, increasing local lattice distortion and suppressing κ . Studies also indicate that replacing Zn with Co in Cu ²ZnSnSe ⁴ increases point defects, reduces phonon relaxation time, and thus decrease κ_1 [63]. Besides, anionic substitution significantly reduces the κ_1 of Cu₂ZnGeSe_{4-x}S_x^[64], primarily due to the disorder caused by substitution. Ultra-low κ_1 can also be achieved in the locally disordered $Cu_{2+x}Zn_{1-x}SnS4^{[43]}$, which is mainly attributed to the highly disordered arrangement of Cu and Zn in the lattice, causing phonon localization and shortening the phonon mean free path. Some researchers also use lattice strain to regulate the thermoelectric properties of materials[65]. They introduce lattice strain by creating dislocations, which reduce the relaxation time of phonons and enhance their scattering, as shown in **Figure 7** .

3.2 Microstructure Design

In addition to introducing point defects, microstructure design, such as nano precipitate, nanocrystalline material, and secondary phase boundary, can also reduce κ ₁. For example, Feng-Jia Fan et al^[66] synthesized Cu₂CdSnSe₄ nanocrystals through colloidal synthesis and prepared bulk materials by hot pressing. In their work, the nanocrystals generated more grain boundaries, significantly enhancing phonon scattering. This ultimately resulted in a thermal conductivity of $1.7 W m⁻¹ K⁻¹$ at room temperature, which is about 40% lower than that of the bulk sample prepared by solidstate reaction. After that, Kaya Wei et al^[67] reported the preparation of nanostructured

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ed nanostructured polycrystals of Cu₂ZnS
 $\$ Cu2ZnSnSe4 and Ag2ZnSnSe4, once again confirming the impact of nanomaterials on the κ_1 of these materials. Combining bulk materials with nanocrystals can reduce thermal conductivity while maintaining the high electrical properties of the bulk material. Qiufan Chen et al^[68] prepared $Cu₂CdSnSe₄$ nanocrystals using colloidal synthesis and added these nanocrystals into the Cu₂CdSnSe₄ matrix, as shown in **Figure 8**. They found that this hierarchical architecture is able to suppress the thermal conductivity while preserving the decent electrical properties. The increased grain boundaries and embedded nanocrystals significantly enhanced phonon scattering, especially the latter serving as additional scattering centers that effectively scatter medium to long wavelength phonons, thereby reducing κ . Himanshu Nautiyal et al^[69] synthesized disordered nanostructured polycrystals of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ through high-energy reaction mechanical alloying, achieving a low thermal conductivity of $0.2 \text{ W m}^{-1} \text{ K}^{-1}$. Similar studies have also been conducted by Binayak Mukherjee et al^[70], who obtained cubic $Cu₂ZnSnSe₄$ nanostructures with a low thermal conductivity of $0.21W$ m⁻¹ K⁻¹.

The optimization of thermal conductivity through grain boundary engineering through the introduction of a secondary phase has also been proven to be an effective method. The interface between the secondary phase and the matrix generates strong phonon scattering. Yingcai Zhu et al^[71] replaced Sn with Pb in $Cu₂ZnSnSe₄$ and found that Pb primarily exists in the PbSe framework, distributed as a secondary phase at grain boundaries, as shown in **Figure 9**. The phase interface between the secondary phase and the matrix has a strong scattering effect on phonons. Additionally, the smaller grain $\mathbf{1}$ $\overline{2}$

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size of the secondary phase increases the density of grain boundaries and further reduces the κ_1 . Furthermore, the composite of CdSe and Cu₂CdSnSe₄ forms a coherent phase interface, allowing charge carriers to pass through while scattering phonons across a wide frequency spectrum^[72]. The Cd vaporization during the hot pressing, creating nanopores in the material that introduce additional scattering centers, significantly reducing the κ .

4 Summary and Outlook

Outlook

Indoid thermoelectric materials have gaine

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III a new star with great researc Recently, diamondoid thermoelectric materials have gained significant attention due to their unique electronic and thermal transport properties. Although their thermoelectric performance has yet to reach the levels of traditional thermoelectric materials, they are still a new star with great research potential. This article focuses on Cu-based quaternary diamondoid materials and provides a collection of recent progress and a comprehensive view of the optimization strategies for improving their electrical and thermal properties. We have thoroughly discussed the influence of various defects on the carrier concentration, carrier mobility and the band structure of the Cu-based quaternary diamondoid materials. Additionally, we have summarized a series of effective methods to enhance the phonon scattering and suppress the thermal conductivity. Overall, improving the carrier mobility while further reducing the thermal conductivity is critical for achieving high thermoelectric performance in these materials. In this context, the recently proposed off-centering effect may offer a new perspective and provide promising pathways for future optimization. In summary, although

significant progress has been made in promoting the thermoelectric performance of these systems, many challenges remain unresolved. We hope this review provide fresh insights and sparks new ideas for further improving the thermoelectric performance of these promising materials.

Competing interests

The authors declare no competing interests.

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Miller Concert Concert Figure 1 The development of quaternary diamondoid thermoelectric materials. (a) Structure of quaternary diamondoid thermoelectric materials. (b) Current state of the art quaternary diamondoid thermoelectric materials, the figure ‐ of ‐ merit *ZT* as a function of temperature and the published time.

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Figure 2 The influence of different cation vacancies on thermoelectric transport properties for Cu ²ZnSnSe ⁴. (a) Schematic diagram of different cation vacancies in Cu₂ZnSnSe₄. Temperature dependence of (b) Electric conductivity (σ) and (c) Lattice thermal conductivity (κ_l) . (d) The room temperature of carrier concentration (p_H) and mobility(μ _H) for different samples. (e) Total thermal conductivity (κ _{tot}) as a function of temperature.

Figure 3 The influence of different defects on carrier transport in $Cu₂FeSnSe₄$. (a) Defect formation energy of Cu-poor conditions. (b) Defect formation energy of Cu-rich conditions. Schematic diagram of charge carriers scattering by (c) V_{Cu} vacancy and (d) Cu_{Fe} anti-site defect. (e) The room temperature carrier concentration (p_H) and mobility (μ_H) for Cu_{2+x}Fe_{1-x}SnSe₄. (f) Electric conductivity (σ) as a function of temperature for $Cu_{2+x}Fe_{1-x}SnSe₄.$

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Figure 4 Introducing graphene to improve the electrical transport performance of Cu ²ZnSnS ⁴. (a) Schematic diagram shows the microstructure of sample. (b) SEM micrographs and TEM image of Cu₂ZnSnS₄/0.75 wt% GNs composite powder. (c) The room temperature carrier concentration (p_H) and mobility (μ_H) of graphene doped samples. (d) Temperature dependence of electric conductivity (σ) .

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Figure 5 The influence of ordered and disordered structure on electrical transport performance of $Cu₂ZnSnS₄$. Temperature dependence of (a) Seebeck coefficient (S) and (b) electric conductivity (σ) . (c) The band structures and density of states for ordered and disordered Cu₂ZnSnS₄.

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Solution of the Mathematical Cu₂ZnSnS₄. (b) Pseudo-culture and disordered cu₂ZnSnS₄. (b) Pseudo-culture T (c/2a) \approx 1. (c) The valence band SS₄. (d) Temperature dependence of ZT is Figure 6 The crystal structure and transport properties of Cu₂ZnSnS₄. (a) The crystal structures of ordered and disordered $Cu₂ZnSnS₄$. (b) Pseudo-cubic structure shows the crystal structure parameter η (c/2a) \approx 1. (c) The valence bands for the ordered and disordered Cu₂ZnSnS₄. (d) Temperature dependence of *ZT* for Cu₂ZnSnS₄ single crystals with different composition.

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Figure 7 The influence of lattice strain on thermal conductivity. (a) The TEM image of Cu2MnSnSe4 showing the stacking faults in the matrix. (b) SAED pattern of Cu2MnSnSe4 along [1 -1 -1] direction. (c) The IFFT image showing dislocation in the material. (d) The corresponding strain mapping of $Cu₂MnSnSe₄$ lattice. (e) The lattice thermal conductivity (κ_1) and lattice strain of Cu₂MnSnSe₄. (f) Temperature dependence of total thermal conductivity (κ_{tot}) of Cu₂MnSnSe₄.

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Figure 8 Morphology and thermal properties of nanocomposite materials. (a) The morphology of fracture surface for Cu ²CdSnSe ⁴ matrix and the nanocomposite. Temperature dependence of (b) total thermal conductivity (κ_{tot}) and (c) lattice thermal conductivity (κ_l) for Cu₂CdSnSe₄ nanocomposite materials.

Figure 9 The structure and thermal properties of Cu₂ZnSn_{1-x}Pb_xSe₄. (a) SEM image of $Cu₂ZnSn_{1-x}Pb_xSe₄$. (b) Schematic diagram of secondary phase boundary scattering. Temperature dependence of (c) total thermal conductivity (κ_{tot}) and (d) lattice thermal conductivity (κ_1) of Cu₂ZnSn_{1-x}Pb_xSe₄.

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Recent Progress on Quaternary Copper-based Diamondoid Thermoelectric Materials

Zihao Zhao¹, Hongyao Xie^{1,*}, Li-Dong Zhao^{1,*}

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g sustainable new energy and high-efficion-
belectric technology has gained attention of
e heat recovery and solid-state refrige
tional thermoelectric materials remains
c elemental composition. Recently, qua
s have garnere **Abstract**: The rising concern on energy and environmental crises have sparked global interest in developing sustainable new energy and high-efficient energy conversion technologies. Thermoelectric technology has gained attention due to its potential for application in waste heat recovery and solid-state refrigeration. However, the application of traditional thermoelectric materials remains limited due to their expensive and toxic elemental composition. Recently, quaternary copper-based diamondoid materials have garnered significant interest due to their unique transport properties, high element abundance, and low toxicity. Many of these materials have demonstrated promising *ZT* value, positioning them as potential candidates for efficient thermoelectric applications. This paper summarizes the recent progress in copper-based quaternary diamondoid materials. We present a collection of research focused on optimizing electrical transport properties through carrier concentration tuning and band engineering, along with an overview of reducing thermal conductivity *via* microstructure enhanced phonon scattering. Finally, we analyze the current research bottlenecks in copper-based quaternary diamondoid thermoelectric materials and propose future research directions.

Keywords: quaternary Cu-based diamondoid materials, thermoelectric performance, carrier concentration, band engineering, microstructure

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1 Introduction

colems. Thermoelectric materials¹²⁻⁴, based
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promising tool for mitigating energy crises
efficiency of thermoelectric materials lin
ons^[6].
Formance of thermoelectric mater The continuous rise in global energy demand and the depletion of unrenewable fossil fuels have made the development of sustainable new energy and high-efficiency energy conversion technologies become the worldwide topics. Research indicates that approximately 65% of energy produced in human activities is wasted and lost as heat^[1]. Thus, developing effective methods to recovery this waste heat is considered as a way to solve the energy problems. Thermoelectric materials $[2-4]$, based on the Seebeck effect, can directly convert heat into electricity, and can also be used for solid state cooling. This makes them a promising tool for mitigating energy crises[5]. However, the low energy conversion efficiency of thermoelectric materials limits their large-scale commercial applications^[6]. tossi hoes have made the development of sustainable new energy and migneenheeley
energy conversion technologies become the worldwide topics. Research indicates that
approximately 65% of energy produced in human activities

Generally, the performance of thermoelectric materials is mainly evaluated by the where *S* is Seebeck coefficient, σ is electrical conductivity, *T* is absolute temperature, κ is electronic thermal conductivity, κ_1 is lattice thermal conductivity, and the sum of κ_{e} and κ_{1} is the total thermal conductivity of the material κ_{tot} ^[7-9] d on the Seebeck effect,
for solid state cooling.
 $s^{[5]}$. However, the low
imits their large-scale
nainly evaluated by the
 $\kappa_{tot} = S^2 \sigma T / (\kappa_e + \kappa_l)$,
s absolute temperature,
ictivity, and the sum of
 $PF = S^2 \sigma$, which is
 a power factor used to characterize the electrical transport performance of thermoelectric materials. Therefore, to improve the performance of thermoelectric materials, two main approaches are typically pursued: (1) optimizing the electrical properties; (2) reducing thermal conductivity^[10, 11]. However, because of the strong inherent coupling between electrical conductivity σ , Seebeck coefficient *S*, and thermal conductivity κ_{tot} , it is challenging to solely regulate these parameters to achieve high

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thermoelectric performance^[12]. For instance, increasing the carrier concentration can enhance σ , but this often reduces the *S* and increases κ _e, limiting the overall improvement in *ZT*. To overcome this, researchers employ various strategies to decouple these properties, aiming for enhanced thermoelectric efficiency.

 $[Q=8, Se, Ie)^{[1/2+2]}$, Zinti phase^[25], Ag₂Q_{26, 27}], half Heusler^[28], and most rece y research on diamondoid compounds principroperties, and their thermoelectric properties for properties, and their thermoelectric Since the discovery of thermoelectric effect, researchers have identified numerous high-performance thermoelectric materials. For example, SnQ ($Q = S$, Se)^[13-16], Bi₂Te₃ alloy^[8, 11, 17, 18], PbQ (Q=S, Se, Te)^[19-22], Zintl phase^[23], Ag₂Q (Q=S, Se, Te)^[24, 25], Mg_3X_2 (X=Sb, Bi)^[26, 27], half Heusler^[28], and most recently, the diamondoid compound[29-32]. Early research on diamondoid compounds primarily concentrated on their optoelectronic properties, and their thermoelectric properties did not receive sufficient attention. Until the excellent thermoelectric properties of Cu₂ZnSnSe₄ and $Cu₂CdSnSe₄$ were first reported by Shi^[33] and Liu et al^[34]. In 2009, diamondoid thermoelectric materials have attracted widespread attention from the research community. Since then, a growing number of wide bandgap diamond-like materials have been reported, such as CuInTe₂, CuGaTe₂, CuFeS₂, Cu₂SnSe₃, Cu₃SbSe₄, etc^{[30,} ³⁵⁻⁴¹. These materials derive from the sphalerite structure and has the typical tetrahedral coordination geometry of diamond. This stable twisted tetrahedral structure is formed by the "cross substitution" of element, following the "eight electron rule". Since the differences in electronegativity and radius between various anions and cations, phonon scattering in this twisted lattice is greatly enhanced, resulting in low κ ¹. This characteristic is important for its decent thermoelectric performance. Quaternary Cubased diamondoid materials generally have a chemical formula of A_2BCQ_4 , with a

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respectives of these materials.
F Ele tetragonal lattice structure that exhibits a double-periodic cubic sphalerite structure along the z-direction, as shown in **Figure 1**. This complex crystal structure and elemental composition result in inherently low κ ¹. In addition, the diverse elemental composition provides it a broad scope to tune the band structure and electrical properties through chemical composition regulation. However, compared to the ternary diamondoid materials, the ZT value of A_2BCQ_4 compounds is lower, typically not exceeding 1.0, mainly due to their lower intrinsic σ . Therefore, a large amount of research aims to improve the electrical properties of quaternary diamondoid materials. Among these materials, Cu-based quaternary diamondoid materials have garnered the most attention. In the next, we start with introducing the recent progress in improving the electronic properties of these materials.

2 Optimization of Electrical Transport Performance

Improving the electrical properties is vital for promoting the thermoelectric performance of quaternary diamondoid materials. However, there is a strong coupling between their σ and S, these parameters are closely related to the carrier concentration and effective mass of the material. The σ is directly proportional to the carrier concentration and mobility: sed quaternary diamondoid materials have garnered the

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n = 4\pi \left(\frac{2m^* k_B T}{h^2}\right)^{\frac{3}{2}} F_{\frac{1}{2}}(\eta)
$$
 (2)

$$
\mu = \frac{2e}{3m^*} \tau_0 \left(\lambda + 1\right) \left(k_B T\right)^{\lambda - \frac{1}{2}} \frac{F_{\lambda}(\eta)}{F_{1/2}(\eta)}\tag{3}
$$

Among formulas, *n* is carrier concentration, μ is carrier mobility, m^* is effective mass of charge carrier, k_B is Boltzmann constant, *h* is planck constant, *n* is simplified Fermi level, τ_0 is relaxation time, λ is scattering factor. Based on the single parabolic band model and the relaxation time approximation, *S* can be derived from the following equation: tion, μ is carrier mobility, m^* is effective mass
ant, h is planck constant, η is simplified Fermi
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 $\frac{e^2 k_B^2 T}{\epsilon h^2} m^$ Materials Lab

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centration, μ is carrier mobility, m^* is effective mass

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S = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}
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4, we can see that optimizing carrier concerned
level can significantly enhance σ . Addition
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djusting the band structure and effective material
of **Carrier Concentratio** From equations 1 to 4, we can see that optimizing carrier concentration by doping and adjusting the Fermi level can significantly enhance σ . Additionally, modifying the density of states by adjusting the band structure and effective mass plays a crucial role in improving the *S*.

2.1 Optimization of Carrier Concentration

Optimizing the carrier concentration is one of the most direct methods to enhance electrical performance. The carrier concentration in a material is influenced by its defect states. Therefore, element doping is a common way to adjust the carrier concentration. Unlike traditional narrow bandgap thermoelectrics ($E_g \le 0.5$ eV), most of Cu-based diamondoid thermoelectric materials exhibit relatively wide bandgaps, E_g > 1eV, as shown in **Table1**. Because of the wide bandgap, most diamondoid materials have intrinsic low carrier concentrations, and element doping is a common and useful method to increase their carrier concentrations and σ .

Recently, many researchers have attempted various doping methods in quaternary

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EXECUTE: Importing Cd with Cu can cu₂CdSnSe₄^[34], substituting Cd with Cu can electrically insulate and $CdSe_4$] units act as the electrically insulate CdSe₄] units act as the electrically insulate Cu can not on diamondoid materials. According to the doping elements, they can be divided into intrinsic and extrinsic doping. Intrinsic doping or self-doping, occurs without introducing any other extrinsic elements, and achieve doping effect by regulating the stoichiometric ratio of the material. In Cu-based diamondoid materials, the predominant charge carriers responsible for electrical transport are holes. Given that the formation energy of copper vacancies is relatively small, these vacancies serve as intrinsic defects significantly influencing the electrical properties of the material. In the early report by Liu et al in 2009 on $Cu_2CdSnSe_4^{[34]}$, substituting Cd with Cu can effectively improve the σ . They found the $\left[\text{Cu}_2\text{Se}_4\right]$ tetrahedral slabs function as electrically conducting units, while the [SnCdSe ⁴] units act as the electrically insulating structures. Thus, introducing excess Cu can not only introduce more intrinsic copper vacancies, generating more holes, but the insulating paths are also transformed into conductive ones due to the replacement of Cd with Cu. As a result, the σ of Cu_{2.1}Cd_{0.9}SnSe₄ achieved an impressive value of 20300 S·m-1 at room temperature, which is about six times higher than that of the pristine sample. The same strategy was successfully applied in another work in 2009^[42], where excess Cu was introduced into $Cu₂ZnSnSe₄$. This result in an impressive σ of 86000 S·m⁻¹ and achieved a groundbreaking *ZT* of 0.91 at 860K. Following these findings, many researchers adopted this strategy to improve the thermoelectric performance of diamondoid materials. For example, Qinghui Jiang et al^[43] prepared $Cu₂ZnSnS₄$ samples using ball milling and hot press methods, and introduced additional Cu into the Zn sites to generate more hole carriers and improve σ . Finally, a high *ZT* value of 1.1 has been achieved for $Cu_{2.125}Zn_{0.875}SnS_4$.

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Besides, Yongkwan Dong et al^[44] explored introducing larger doses of Cu to further improve the σ of the material. Although introducing more low-valence cations at high valence sites has been proven to be an effective means of improving σ excessive doping can easily lead to the formation of secondary phases. To address this, Zhou Li et al[45] explored optimizing the carrier concentration by constructing different cation vacancies in Cu₂ZnSnSe₄, as shown in **Figure 2**. They studied the effects of three types of cationic vacancies, Cu, Zn, and Sn, on electrical properties, and found that all samples exhibited a significant increase in hole concentration compared to the pristine samples. Notably, the Sn-deficient sample achieved the highest carrier concentration of 7.5×10^{19} cm⁻³, resulting in an σ of 4700 S·m⁻¹.

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ignificant increase in hole concentration contents.
The Sn-deficient sample achieved the highest comparent and σ of 4700 S·m⁻¹.
Trinsic doping, introducing extrinsic elem In addition to intrinsic doping, introducing extrinsic elements to increase the carrier concentration is a commonly used and effective optimization method. For example, X. Y. Shi et al^[33] attempted to dope In at Sn site in Cu₂ZnSnSe₄, achieving a high carrier concentration that significantly improved the σ of the material, resulting in a record high *ZT* of 0.95 at 850K. Similarly, F. S. Liu et al^[46] explored the role of doping Mn at Cd site in $Cu₂CdSnSe₄$ through experiment and theoretical calculation. They found that Mn doping causes the Fermi level to shift towards the valence band, resulting in a higher hole concentration while the carrier mobility decreases with increasing Mn content, ultimately leading to an increase in σ . Bo Wang et al^[47] also achieved a similar effect by doping Ga at the Sn site in Cu₂CdSnSe₄. This strategy was also used in $Cu_2CdSn_{0.9}In_{0.1}Se_4^{[48]}$, $Cu_2MnSn_{0.95}In_{0.05}Se_4^{[49]}$ and $Cu_2ZnSn_{0.95}Ga_{0.05}Se_4^{[50]}$, further demonstrating the effectiveness of extrinsic doping in enhancing the thermoelectric $\mathbf{1}$

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performance of quaternary diamondoid materials.

2.2 Optimization of Carrier Mobility

FeSnSe₄. They calculated the defect formation
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the conditions and identified the domination
ase of Cu deficiency (**Figure 3a**), the defective, indicating that Cu vacancies It is well known that, the carrier mobility of a material is closely related to the effective mass and scattering mechanisms. Therefore, a large amount of research on carrier mobility optimization has focused on these aspects. For example, Q. Song et $al^{[51]}$ optimized the lower intrinsic mobility of materials by manipulating the intrinsic lattice defects in Cu ²FeSnSe ⁴. They calculated the defect formation energies under both Cu-poor and Cu-rich conditions and identified the dominated defect types in Cu ²FeSnSe ⁴. In the case of Cu deficiency (**Figure 3a**), the defect formation energy of Cu vacancies is negative, indicating that Cu vacancies spontaneously occur during material preparation. Since the Cu vacancy is electronegative, making them to disrupt the original periodicity of the lattice and introduce additional ionized impurity scattering centers, thus reducing the carrier mobility, as shown in **Figure 3c**.

In contrast, they found that under Cu-rich condition, the defect formation energy of Cu atoms occupying Fe sites (Cu_{Fe} anti-site defect) is lower than that of Cu vacancies, indicating the Cu_{Fe} anti-site defect is dominant, as shown in **Figure 3b**. This defect is almost electrically neutral, so it causes only minimal disruption to the charge transport (**Figure 3d**). As a result, carrier mobility is less affected by scattering. Through carefully controlling the Cu content, they successfully achieved a synergistic optimization of both carrier mobility and carrier concentration, as shown in **Figure 3e**. And ultimately, it increased the conductivity of the material by about 2.5 times, as

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shown in **Figure 3f.** Furthermore, doping In into Cu₂MnSnSe₄ can also improve the carrier mobility of the material^[49]. This enhancement may be attributed to the optimization of band structure. In addition, by studying the transport properties of $Cu_2CoSnSe_4$ and Cu_2CoSnS_4 . Taras Parashchuk et al^[52] found that the selenide compound exhibited higher symmetry than its sulfide analogue, featuring with the bond angles closer to the ideal tetrahedral angle of 109.5°, this contribute to a higher carrier mobility.

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The increase in σ is attributed to the for

the 2D graphene, which facilitates the Improving the electrical transport properties by introducing a secondary phase is a novel method. For example, Sarita Devi Sharma et al^[53] improved the thermoelectric properties of $Cu₂ZnSnS₄$ by adding graphene nanosheets (GNs) into the matrix, as shown in **Figure 4**. The increase in σ is attributed to the formation of percolation channels created by the 2D graphene, which facilitates the transport of charge carriers. In this case, even small amount of GNs can produce a significant percolation effect. Additionally, the graphene nanosheets can exhibit a doping effect and moderately increase the carrier concentrations of the material.

Similarly, Arslan Ashfaq et al^[54] prepared a series of Al-doped $Cu₂ZnSnS₄$ nanoparticles using the hydrothermal method, and found the extra Al effectively increases the σ of the material. This is because a small amount of Al particles diffuses into the gap of the matrix, forming bridge that allow charge carriers to pass freely through the grain boundaries, thus, increase the carrier concentration and mobility simultaneously.

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2.3 Optimization of Seebeck Coefficient

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sotta et al^[55] demonstrated that the transition
n Cu₂ZnSnS₄ improves the thermoelectr The *S* is closely related to the density of states effective mass and carrier concentration. Although reducing carrier concentration is able to increase the *S*, it simultaneously lowers the σ . Therefore, band structure optimization emerges as a practical option to boost the S without compromising the σ . Cu-based quaternary diamondoid materials can exhibit two distinct crystal structures, the highly ordered Stannite and the disordered Kesterite. The symmetry of these crystal structures directly impacts the band structure of materials. Various methods have been developed to optimize the band structure and transport properties through manipulating the crystal structure. Eleonora Isotta et al^[55] demonstrated that the transition from an ordered to a disordered structure in Cu₂ZnSnS₄ improves the thermoelectric properties of materials, primarily due to alterations in the electronic band structure as shown in **Figure 5**. They found a second-order reversible phase transition occurring near 533K. **Figure 5a** shows that the *S* increases sharply around the transition temperature, attributed to the higher symmetry associated with the disordered structure. At the same time, the σ of the material dramatically drops at the phase transition temperature, as shown in **Figure 5b**. Through the electronic band calculation, they found that in disordered structures, the energy difference among the first three valence bands decrease, the top of the valence band flattens, and the band gap also decreases, as shown in the **Figure 5c**. Following this, Akira Nagaoka et al^[56] employed a pseudo-cubic strategy to enhance the thermoelectric performance of Cu ²ZnSnS ⁴ single crystal, as shown in **Figure 6**. They obtained the degenerate electron energy bands in the pseudo-cubic structure, resulting

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in a high *S* and a remarkable *ZT* value of 1.6 at 800K in the material.

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of σ were improved. Jolly Jacob et al^[58] add
u₂ZnSnS₄ and found that the *S* In addition, several methods can effectively improve the *S* of materials without altering their band structure. For example, by introducing energy barriers at the interface through doping or incorporation of secondary phase, low-energy carriers would be greatly scattered while high-energy carriers can pass through, achieving the goal of improving *S*. Qiufan Chen et al^[57] doped Ag atoms into Cu₂CdSnSe₄ using a chemical method, successfully embedding a disordered sphalerite structure within the ordered sphalerite phase. This modification caused the energy band at the interface to bend, thereby generating energy barriers that effectively scatter low-energy carriers. As a result, both the *S* and σ were improved. Jolly Jacob et al^[58] adopted a similar strategy by doping Cd into Cu2ZnSnS4 and found that the *S* increased with adding Cd. They found that, Cd doping led to the formation of Cu-based secondary phases. These secondary phases serve as effective filters for low-energy carriers, while allowing only high-energy carriers to pass through, thereby improving the performance of material. Additionally, introducing spin entropy by doping magnetic particles such as Ni^[59] or elements such as Pb and Te^[60] can effectively increase the effective mass and improve the *S* of the material.

3 Optimization of Thermal Transport Performance

We know that the transfer of thermal energy is mainly achieved through lattice vibrations and carrier transport, with the former represented as lattice thermal conductivity κ_1 and the latter as electronic thermal conductivity κ_e . They can be 123456789

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collision^[61], *L* is Lorentz constant. Although the In the above equation, C_v is specific heat at constant volume of materials, v is phonon velocity, l is mean free path of phonon collision^[61], L is Lorentz constant. Although the complex crystal structure and elemental composition of Cu-based quaternary diamondoid materials result in relatively low intrinsic thermal conductivity, there is still room for further optimization. Unlike κ _e, κ _l is almost independent of other electronic transport parameters, and can be regulated independently. To this end, many researchers have focused on reducing the κ ¹ to improve the thermoelectric performance. Defect control and microstructure design are two effective methods for reducing κ ¹.

3.1 Defect Control

Compared to C_v and v , the *l* is easier to regulate, particularly through controlling the defects state in the material. So far, introducing appropriate defects into the lattice to reduce the l has remained the main strategy for suppressing κ_l . The impact of point defects mainly lies in the fluctuation of the mass field caused by different atomic masses and the fluctuation of the stress field caused by different atomic radii. The larger the difference, the stronger the scattering effect on high-frequency phonons, and the better the result in reducing κ ¹. For example, Qiufan Chen et al^[57] prepared Ag-doped $Cu₂CdSnSe₄$ using a chemical method, which introduced Ag_{Cu} point defects into the This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

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Fred Cu_{2+x}Zn_{1-x}SnS₄⁺⁺²¹, which is mainly a
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which reduce the relaxation time of p matrix, distorting the crystal structure and enhancing the phonon scattering. In addition, Qingfeng Song et al^[62] introduced excess Cu into $Cu₂MnSnSe₄$, increasing local lattice distortion and suppressing κ ¹. Studies also indicate that replacing Zn with Co in Cu2ZnSnSe4 increases point defects, reduces phonon relaxation time, and thus decrease κ_1 ^[63]. Besides, anionic substitution significantly reduces the κ_1 of Cu₂ZnGeSe_{4-x}S_x^[64], primarily due to the disorder caused by substitution. Ultra-low κ ¹ can also be achieved in the locally disordered $Cu_{2+x}Zn_{1-x}SnS4^{[43]}$, which is mainly attributed to the highly disordered arrangement of Cu and Zn in the lattice, causing phonon localization and shortening the phonon mean free path. Some researchers also use lattice strain to regulate the thermoelectric properties of materials^[65]. They introduce lattice strain by creating dislocations, which reduce the relaxation time of phonons and enhance their scattering, as shown in **Figure 7**.

3.2 Microstructure Design

In addition to introducing point defects, microstructure design, such as nano precipitate, nanocrystalline material, and secondary phase boundary, can also reduce κ ₁. For example, Feng-Jia Fan et al^[66] synthesized Cu₂CdSnSe₄ nanocrystals through colloidal synthesis and prepared bulk materials by hot pressing. In their work, the nanocrystals generated more grain boundaries, significantly enhancing phonon scattering. This ultimately resulted in a thermal conductivity of $1.7 W m⁻¹ K⁻¹$ at room temperature, which is about 40% lower than that of the bulk sample prepared by solidstate reaction. After that, Kaya Wei et al^[67] reported the preparation of nanostructured $\mathbf{1}$

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ed nanostructured polycrystals of Cu₂Z Cu₂ZnSnSe₄ and Ag₂ZnSnSe₄, once again confirming the impact of nanomaterials on the κ_1 of these materials. Combining bulk materials with nanocrystals can reduce thermal conductivity while maintaining the high electrical properties of the bulk material. Qiufan Chen et al^[68] prepared Cu₂CdSnSe₄ nanocrystals using colloidal synthesis and added these nanocrystals into the Cu ²CdSnSe ⁴ matrix, as shown in **Figure 8**. They found that this hierarchical architecture is able to suppress the thermal conductivity while preserving the decent electrical properties. The increased grain boundaries and embedded nanocrystals significantly enhanced phonon scattering, especially the latter serving as additional scattering centers that effectively scatter medium to long wavelength phonons, thereby reducing *k*l . Himanshu Nautiyal et al[69] synthesized disordered nanostructured polycrystals of Cu₂ZnSnS₄ and Cu₂ZnSnSe₄ through high-energy reaction mechanical alloying, achieving a low thermal conductivity of $0.2 \text{ W m}^{-1} \text{ K}^{-1}$. Similar studies have also been conducted by Binayak Mukherjee et al^[70], who obtained cubic $Cu₂ZnSnSe₄$ nanostructures with a low thermal conductivity of $0.21W$ m⁻¹ K⁻¹.

The optimization of thermal conductivity through grain boundary engineering through the introduction of a secondary phase has also been proven to be an effective method. The interface between the secondary phase and the matrix generates strong phonon scattering. Yingcai Zhu et al^[71] replaced Sn with Pb in Cu₂ZnSnSe₄ and found that Pb primarily exists in the PbSe framework, distributed as a secondary phase at grain boundaries, as shown in **Figure 9** . The phase interface between the secondary phase and the matrix has a strong scattering effect on phonons. Additionally, the smaller grain
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size of the secondary phase increases the density of grain boundaries and further reduces the κ ¹. Furthermore, the composite of CdSe and Cu₂CdSnSe₄ forms a coherent phase interface, allowing charge carriers to pass through while scattering phonons across a wide frequency spectrum^[72]. The Cd vaporization during the hot pressing, creating nanopores in the material that introduce additional scattering centers, significantly reducing the κ ¹.

4 Summary and Outlook

Outlook

Indoid thermoelectric materials have gaine

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III a new star with great researc Recently, diamondoid thermoelectric materials have gained significant attention due to their unique electronic and thermal transport properties. Although their thermoelectric performance has yet to reach the levels of traditional thermoelectric materials, they are still a new star with great research potential. This article focuses on Cu-based quaternary diamondoid materials and provides a collection of recent progress and a comprehensive view of the optimization strategies for improving their electrical and thermal properties. We have thoroughly discussed the influence of various defects on the carrier concentration, carrier mobility and the band structure of the Cu-based quaternary diamondoid materials. Additionally, we have summarized a series of effective methods to enhance the phonon scattering and suppress the thermal conductivity. Overall, improving the carrier mobility while further reducing the thermal conductivity is critical for achieving high thermoelectric performance in these materials. In this context, the recently proposed off-centering effect may offer a new perspective and provide promising pathways for future optimization. In summary, although

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significant progress has been made in promoting the thermoelectric performance of these systems, many challenges remain unresolved. We hope this review provide fresh insights and sparks new ideas for further improving the thermoelectric performance of these promising materials.

Competing interests

The authors declare no competing interests.

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Miller Review Only Figure 1 The development of quaternary diamondoid thermoelectric materials. (a) Structure of quaternary diamondoid thermoelectric materials. (b) Current state of the art quaternary diamondoid thermoelectric materials, the figure ‐ of ‐ merit *ZT* as a function of temperature and the published time.

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Figure 2 The influence of different cation vacancies on thermoelectric transport properties for Cu₂ZnSnSe₄. (a) Schematic diagram of different cation vacancies in Cu₂ZnSnSe₄. Temperature dependence of (b) Electric conductivity (σ) and (c) Lattice thermal conductivity (κ_l) . (d) The room temperature of carrier concentration (p_H) and mobility(μ_H) for different samples. (e) Total thermal conductivity (κ_{tot}) as a function of temperature.

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 E_{form} (eV)

Fe-Sn

 Cu_F

Cu-Sn

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 E_f (eV)

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 V_{Fe}

Cu rich

Cu

charged

Cu_{2+v}Fe_{1+v}SnSe

Figure 4 Introducing graphene to improve the electrical transport performance of Cu2ZnSnS4. (a) Schematic diagram shows the microstructure of sample. (b) SEM micrographs and TEM image of $Cu₂ZnSnS₄/0.75$ wt% GNs composite powder. (c) The room temperature carrier concentration (p_H) and mobility (μ_H) of graphene doped samples. (d) Temperature dependence of electric conductivity (σ) .

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Figure 5 The influence of ordered and disordered structure on electrical transport performance of Cu ²ZnSnS ⁴. Temperature dependence of (a) Seebeck coefficient (S) and (b) electric conductivity (σ) . (c) The band structures and density of states for ordered and disordered Cu₂ZnSnS₄.

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Solution of the Mathematical Cu₂ZnSnS₄. (b) Pseudo-culture and disordered cu₂ZnSnS₄. (b) Pseudo-culture T (c/2a) \approx 1. (c) The valence band SS₄. (d) Temperature dependence of ZT is **Figure 6** The crystal structure and transport properties of Cu₂ZnSnS₄. (a) The crystal structures of ordered and disordered $Cu₂ZnSnS₄$. (b) Pseudo-cubic structure shows the crystal structure parameter η (c/2a) \approx 1. (c) The valence bands for the ordered and disordered Cu₂ZnSnS₄. (d) Temperature dependence of *ZT* for Cu₂ZnSnS₄ single crystals with different composition.

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Figure 7 The influence of lattice strain on thermal conductivity. (a) The TEM image of Cu ²MnSnSe4 showing the stacking faults in the matrix. (b) SAED pattern of Cu ²MnSnSe4 along [1 -1 -1] direction. (c) The IFFT image showing dislocation in the material. (d) The corresponding strain mapping of Cu₂MnSnSe₄ lattice. (e) The lattice thermal conductivity (κ_1) and lattice strain of Cu₂MnSnSe₄. (f) Temperature dependence of total thermal conductivity (κ_{tot}) of Cu₂MnSnSe₄.

Figure 8 Morphology and thermal properties of nanocomposite materials. (a) The morphology of fracture surface for Cu₂CdSnSe₄ matrix and the nanocomposite. Temperature dependence of (b) total thermal conductivity (κ_{tot}) and (c) lattice thermal conductivity (κ_1) for Cu₂CdSnSe₄ nanocomposite materials.

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Figure 9 The structure and thermal properties of $Cu₂ZnSn_{1-x}Pb_xSe₄$. (a) SEM image of $Cu₂ZnSn_{1-x}Pb_xSe₄$. (b) Schematic diagram of secondary phase boundary scattering. Temperature dependence of (c) total thermal conductivity (κ_{tot}) and (d) lattice thermal conductivity (κ_1) of Cu₂ZnSn_{1-x}Pb_xSe₄.

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