## Insights into the Classification of Nanoinclusions of Composites for Thermoelectric Applications

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**ABSTRACT:** Thermoelectric composites are known for their enhanced power conversion performance via interfacial engineering and intensified mechanical, structural, and thermal properties. However, the selection of these nanoinclusions, for example, their type, size effect, volume fraction, distribution uniformity, coherency with host, carrier dynamics, and physical stability, plays a crucial role in modifying the host material thermoelectric properties. In this Review, we classify the nanoinclusions into five types: carbon allotropes, secondary thermoelectric phases, metallic materials, insulating oxides, and others. On the basis of the classification, we discuss the mechanisms involved in improving the *ZT* of nanocomposites involving reduction of thermal conductivity ( $\kappa$ ) by phonon scattering, improving the Seebeck coefficient ( $\alpha$ ) via energy filtering effect and the



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electrical conductivity ( $\sigma$ ) by carrier injection or carrier channeling. Comprehensibly, we validate that adding nanoinclusions with high electrical and low thermal conductivity as compared to the matrix material is the best way to optimize the interlocked thermoelectric parameters. Thus, collective doping and nanoinclusions in thermoelectric materials is the best possible solution to achieve a higher power conversion efficiency equivalent to other renewable energy technologies.

**KEYWORDS:** nanoinclusion, thermoelectrics, nanocomposites, phonon scattering, energy filtering

#### INTRODUCTION

The growing interest in developing decarbonization technologies and tremendous demand for sustainable energy sources drives the world toward substitutions for fossil fuel resources. Globally, fossil fuel-based energy consumption is almost 85% of the sustainable energy sources, which leads to uncontrolled environmental pollution and global warming. Out of the total energy consumption, nearly 70% of energy is released in the form of waste heat; as a result, explorations directed toward the effective recycling of heat energy are gaining more importance.<sup>1</sup> In this aspect, a thermoelectric generator (TEG) is one of the eco-friendly and renewable energy resources that directly generates electricity from recycling waste heat. However, the efficiency of TEGs is still trailing behind other energy conversion technologies; thus, to improve their conventional device efficiency by >15% and gain longterm reliability, strategies to develop high-performance materials are underway.<sup>2</sup> The thermoelectric figure of merit can be measured by the formula,  $ZT = \alpha^2 \sigma T / \kappa$ , where  $\alpha$  is the Seebeck coefficient, *T* is the absolute temperature, and  $\sigma$  and  $\kappa$ are the electrical and thermal conductivities, respectively.<sup>3</sup> Recently, the development of TE materials has mainly focused on nanoengineering, defect engineering, and band engineering strategies. Generally, the thermoelectric performance of a

material can be enhanced either by increasing its  $\sigma$  or  $\alpha$  or by reducing  $\kappa$ .<sup>4</sup> The  $\sigma$ ,  $\alpha$ , and  $\kappa$  values are inversely dependent on the charge carrier concentration, and optimizing them individually through altering the carrier concentration is nearly impractical. However, thermal conductivity consists of two contributors ( $\kappa$ ): (i) lattice or phonon thermal conductivity  $(\kappa_{\rm p})$  and (ii) electron thermal conductivity  $(\kappa_{\rm e})$ . To reduce the total  $\kappa$ , current studies only concentrate on phonon scattering to reduce  $\kappa_{\rm p}$  as the reduction of  $\kappa_{\rm e}$  also reduces the  $\sigma^{1}$ . Recent thermoelectric studies focus on decoupling the interlocked thermoelectric parameters using the band or defect engineering to increase the power factor ( $PF = \alpha^2 \sigma$ ), and nanoengineering to reduce the  $\kappa$ <sup>5,6</sup> A good thermoelectric material should have a high structural complexion to reduce  $\kappa$ , a high carrier mobility to improve  $\sigma$ , and a large effective mass to enhance  $\alpha$ . Improving the ZT through optimizing the PF is pretty complex in this direction, as both  $\sigma$  and  $\alpha$  are inversely proportional to

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Figure 1. (a) Number of publications per year on thermoelectric composites with the inset showing publication count per 6 years. (b) Various types of nanoinclusions-associated thermoelectric articles were published in 2021 (the plotted data in both graphs are collected from the Web of Science database using the keywords thermoelectric and composite).



Figure 2. Schematic diagram showing the possible ZT-improving mechanisms associated with thermoelectric nanocomposite materials.

the carrier concentration. Therefore, reducing the  $\kappa$  via nanoengineering without impacting the PF is an effective alternate way to improve ZT.<sup>5</sup>

Nanoengineering is performed by nanocompositing or developing nanograin structures in the thermoelectric matrix. Favier et al. demonstrated that nanocompositing-associated lattice interfaces scatter thermal carriers more effectively than do grain boundaries. Therefore, adding nanoinclusions is better than producing nanograin structures to improve ZT.<sup>8</sup> Thus, nanocompositing is one of the best strategies for modifying the interconnected  $\sigma$ ,  $\alpha$ , and  $\kappa$ .<sup>4</sup> In this direction, the *PF* is improved by controlling the transport channel for charge carriers while reducing the lattice thermal conductivity by induced phonon scattering.<sup>9</sup> In recent years, the research community has shown strong interest in thermoelectric composites, which we keenly observe statistically from the number of articles published per year, as shown in Figure 1a. A tremendous increase in the number of articles published in the last six years (2016-21) is nearly 60% of the overall published articles from 1992, as shown in the inset of Figure 1a.

Nanocompositing primarily scatters the phonons by employing interfacial engineering to reduce  $\kappa$  by reducing the phonons' mean free path, as shown in Figure 2.<sup>10</sup> These nanoinclusions inhibit grain growth of the matrix and then produce the fine-grain boundaries, and the resulting newly formed interfaces are strongly scattering the phonons and reducing their phonon lifetime.<sup>11–16</sup> The total phonon relaxation time  $\tau_{\rm T}$  can be expressed as in eq 1:<sup>17</sup>

$$\frac{1}{\tau_{\rm T}} = \frac{1}{\tau_{\rm PD}} + \frac{1}{\tau_{\rm NP}} + \frac{1}{\tau_{\rm U}} + \frac{1}{\tau_{\rm GB}} + \frac{1}{\tau_{\rm SF}}$$
(1)

where  $au_{\rm PD}$ ,  $au_{\rm NP}$ ,  $au_{\rm U}$ ,  $au_{\rm GB}$ , and  $au_{\rm SF}$  are the relaxation times corresponding to scattering from the point defects, nanoinclusions, phonon-phonon Umklapp process, grain boundaries, and stacking faults, respectively. Robust phonon-phonon scatterings, reduction of phonon velocities, and acoustic and optical phonon modes' interaction help in achieving an ultralow lattice thermal conductivity.<sup>18</sup> The nanoinclusion phase effectively reduces the relaxation time of the phonons in a wider frequency range than do other types of scattering points (i.e., grain boundary, phonon-phonon, point defect, or stacking fault), as demonstrated in Figure 3c. The nanoinclusions are more potent in reducing the phonons' relaxation time, especially in the low frequency range, than are grain boundaries and point defects, as shown in Figure 3d. Generally, electrons' mean free paths are shorter than the phonons' mean free paths; therefore, adding nanoinclusionsbased interfaces makes phonons' scattering much more effective than charge carriers.<sup>2,19</sup> Nanoinclusion sites primarily act as phonon scattering centers to scatter heat-carrying phonons by generating fine-grain boundaries and structural deformities (point and line defects), in turn reducing  $\kappa$  further. Phonon scattering strongly occurs when the phonon wavelengths are comparable to the nanoparticles' size, which would play a vital role because in this range the phonon frequencies typically cannot be effectively scattered by either point defects



**Figure 3.** (a) Variation in the thermoelectric parameters employing carrier concentration. (b) Seebeck distribution concerning the energy of carriers with the inset showing the energy filtering mechanism. Reprinted with permission from ref 26. Copyright 2009 Royal Society of Chemistry. (c) Phonons frequency relaxation time reduction by various scattering phenomena. Reprinted with permission from ref 36. Copyright 2022 Springer Nature. (d) Relaxation time as a function of phonon frequency for different scattering mechanisms. (e) Estimation of the relaxation time by various sizes of nanoinclusions by fixing the weight percentage. Reprinted with permission from ref 20. Copyright 2020 Elsevier. (f) Thermal conductivity of the SiGe nanocomposite with cylindrical inclusions predicted with unmodified effective medium approximation (EMA) formulation. Reprinted with permission from ref 37. Copyright 2007 AIP Publishing.

or grain boundaries.<sup>20</sup> Nanoinclusions-associated interface boundaries scatter high-frequency phonons, whereas the induced structural defects and fine grain boundaries scatter short- and mid-frequency phonons, respectively.<sup>21,22</sup> Advantageously, these nanoinclusions also act as back stress points during densification, which makes some percentage of enhancement in porosity as compared to pristine materials, that is also attributed to the reduced  $\kappa$ .<sup>23–25</sup>

Minnich et al.<sup>26</sup> calculated the Seebeck coefficient ( $\alpha$ ) distribution concerning their carrier energy, as shown in Figure 3b, which indicates that the presence of low-energy carriers reduces the overall  $\alpha$  in the material. Similarly, adding nanoinclusions also scatters the low-energy carriers, which responsibly improves the  $\alpha$  by acting as charge carrier filters, as depicted in Figure 2.<sup>5,13,23,27–34</sup> However, the addition of nanoinclusions also results in band bending at interface boundaries, which creates a potential barrier to low-energy carriers, thereby allowing the high-energy carriers to transport, as shown in the inset of Figure 3b.<sup>35</sup> This mechanism is called carrier energy filtering, influenced by enhancing the carriers' effective mass, as per the Pisarenko relation  $\alpha \propto \frac{m^*}{2/3}$ , where *n* is the carrier concentration and  $m^*$  is the effective mass of the carriers. As a result, low-energy carrier filtering reduces the mean free path electrons and increases the carriers' effective mass, improving  $\alpha$ . Hong et al.<sup>38</sup> determined the golden range of the Seebeck coefficient and the associated lattice thermal conductivity to achieve a maximized ZT. This specific range is easily achieved by nanocompositing, by means of controlling and optimizing the energy filtering and phonon scattering mechanisms.

In the prospect of electrical conductivity ( $\sigma$ ), the effect of nanoinclusion on the improvement of  $\sigma$  depends on the matrix's band structure and the nanoinclusion phase's electrical conductivity. Generally, semiconducting nanoinclusions are aimed to improve the electrical conductivity by employing carrier channeling or carrier injection mechanisms. Band splitting due to the Rashba effect (atomic displacement) helps in enhancing electrical transport, and then, together with the presence of nanoprecipitates, helps in achieving an ultralow lattice thermal conductivity, which when combined together aids in maximizing the ZT.<sup>39</sup> In nanocomposites, in most cases,  $\sigma$  decreases due to the reduction of the mobility of carriers dominated by the interfaces and the neutralization due to the carrier concentration of the nanoinclusion phase.<sup>40</sup> However, the higher porosity from nanocompositing affects their electrical properties, significantly reducing the  $\sigma$ .<sup>41</sup> Substantial uncertainty in  $\sigma$  and  $\alpha$  is commonly observed in the nanocomposite structures; however, this does not cause a negative effect on the power factor.

As mentioned earlier, grain boundaries are primarily helpful for phonon scattering as compared to electron scattering as band bending occurs near microscale boundaries.<sup>42</sup> The structural factors such as nanoinclusion distribution and the associated boundary scales such as a microscale matrix or a nanoscale matrix with nanoinclusions vary on the basis of the synthesis technique and sintering temperature. However, in nanoscale boundaries, charge carrier scattering caused by boundaries is overshadowed by the reduction of the carriers' mobility, nullifying their effect on *PF*.<sup>4,6</sup> In nanocomposites, a micromatrix is preferable because charge carriers choose a low resistivity path, and nanoinclusions are preferable because the phonon does not select any path and travel in random



Figure 4. (a) Uniform distribution and multisize. (b) Uniform distribution and homosize. (c) Nonuniform distribution and multisize are three possible microstructures of nanoinclusion size and distribution combinations in the nanocomposites.

directions.<sup>4</sup> Therefore, combining a micromatrix with nanoinclusions is an excellent approach to decoupling the interlocked thermoelectric parameters simultaneously.<sup>4,42</sup> The other advantages of nanocompositing are improving the thermal, phase stability, and mechanical properties of the thermoelectric materials.<sup>11,32,43–46</sup>

To summarize, nanocompositing is one of the best strategies for attaining an ultralow  $\kappa$  as it offers the combined effects of interfaces, fine grain boundaries, and complex structural defects.<sup>11,47,48</sup> An optimum concentration of nanoinclusions with excellent  $\sigma$  and thermal resistivity higher than that of the matrix will be the best choice to produce a high ZT.<sup>49,50</sup> In this Review, we try to summarize the advantages of nanocomposites experienced in various thermoelectric host materials. We also emphasize this technique as a facile way to improve their power conversion efficiencies irrespective of their inherited properties.

#### KEY FACTORS FOR THE SELECTION OF NANOINCLUSIONS

The critical aspect in selecting nanoinclusions depends on the thermoelectric matrix's electrical and thermal properties to develop into a composite structure. Besides the matrix properties, the selection of nanoinclusions also depends on many factors such as the type of nanoinclusion, size effect, concentration, distribution, carrier transport, lattice coherence, and physical stability.<sup>5,51–53</sup>

**Types of Nanoinclusions.** Generally, semiconductive nanoinclusions enhance *S* by energy filtering and/or  $\sigma$  by carrier channeling or injection and reduce  $\kappa$  by phonon scattering. In this Review, we classify the nanoinclusions into five significant types for forming thermoelectric nanocomposites, which are discussed in a later section (Classification of Nanoinclusions).

Size Effect of Nanoinclusions. The size of the nanoinclusion is one of the primary parameters in thermoelectric composites as both electrons' and phonons' scattering depends mainly on the length of the interface boundaries.<sup>6,52,54</sup> As the phonons' mean free path (mfp) typically ranges in a few nanometers, nanocomposites offer the possibility for effectively scattering phonons with a long mfp without hindering the electrical conduction. Lee et al.<sup>20</sup> estimated that, from many studies, it is determined that the size of the nanoinclusions should be as low as 50 nm to maximize the phonon scattering and minimize the charge carrier scattering effectively. It is also estimated that the thermal conductivity reduces further, employing reduction in the phonon relaxation time as the size of the nanoinclusions decreased as low as 5-10 nm, as shown in Figure 3e.<sup>20</sup> Figure 3f shows that nanocomposites with a higher interface density strongly reduce their effective thermal conductivity as the inclusion size is smaller than the

phonon mfp.37 In addition, discovered phonons with wavelength similar to the size of the nanoinclusions were extensive scattered. Therefore, 3D nanoparticle scattering is a sizeresonance scattering, which strongly scatters phonons with a low frequency rather than a high frequency.<sup>54</sup> Tarkhanyan et al.<sup>51</sup> demonstrated that a lower diameter of the selected nanoinclusions for a given concentration and temperature attains an effective decrease in the lattice thermal conductivity. Yang et al.<sup>53</sup> explained that optimum multisize (below mfp of phonons) particles better scatter multifrequency phonons to reduce the thermal conductivity than do uniform size particles. Thus, the size of the nanoinclusions is crucial and optimum as large nanoinclusions influence dense scattering of the electrical carriers, reducing the PF.<sup>28,30,55,56</sup> Smaller nanoinclusions show a more significant reinforcement and toughening effect to improve the mechanical stability than do the large nanoinclusions.<sup>5</sup>

Concentration of Nanoinclusions. The concentration of the nanoinclusions should be calculated to an optimum level such that the composite should have a negotiable effect on electrical transport and a maximum impact on reducing  $\kappa$ .<sup>56</sup> Nanoinclusion concentrations around 5–6 wt % are estimated as optimized to form uniform dispersoids around the grain boundaries and form into a composite structure with maximum TE performance.<sup>58,59</sup> For example, adding 3 vol % Ag nanoinclusions in the oxide matrix increases the  $\kappa$  twice and reduces the overall ZT.<sup>24</sup> With the increasing nanoinclusion concentration, their corresponding inclusion size also increases, negatively affecting the material ZT, that is, reducing the mean free path of the electrons and the PF.<sup>52</sup> The addition of a high concentration of nanoinclusions causes an agglomerate at the grain boundaries during sintering and has detrimental effects on the thermoelectric performance.<sup>46,60,61</sup> The added meager amount nonetheless reacts with the matrix phase to create any other secondary phases.<sup>31,32,62</sup>

**Distribution of Nanoinclusions.** Generally, nanoinclusions preferably settle down at the grain boundaries in composite materials, and their uniform distribution improves phonon scattering over the clustered nonuniform distribution.  $^{5,27-30,53,58,62-64}$  In situ nanoinclusions distribute uniformly throughout the grains, whereas ex situ nanoinclusions settle along the grain boundaries. <sup>65</sup> Figure 4 shows the three possible microstructures of the nanoinclusions' distribution and the particle size combinations in the nanocomposites. Most studies report that the interfacial boundaries of homogeneously dispersed nanoinclusions effectively scatter phonons more than do the electrons. <sup>28,55</sup> Therefore, the best possible combination is the homogeneous distribution with optimum multisize nanoinclusions to attain a maximum *ZT*, as shown in Figure 4a. However, the distribution of nano-inclusions also affects their mechanical properties as finely

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Figure 5. Schematic illustration of the popular synthesis routes for thermoelectric nanocomposites.

 Table 1. Some of the Enormously Improved ZT Composites by the Addition of the Optimum Amount of Nanoinclusions at

 Their Peak Applicable Temperatures

matrix	inclusion	synthesis	$\sigma$ (%)	α (%)	κ (%)	ZT (%)	ref
Cu <sub>3</sub> SbS <sub>4</sub>	carbon black	BM+HP	-58	48	-49	173	73
$Cu_2ZnSnS_4$	graphene	ST+HP	1250	-44	-4	614	77
Cu <sub>2</sub> Se	graphene	BM+melt	-33	6	-220	144	78
SnTe	WSe <sub>2</sub>	BM+HP	-3	14	-52	134	36
Ag <sub>2</sub> Se	Cu <sub>2</sub> Se	BM+SPS	14	4	-31	120	45
РЬТе	Cu <sub>2</sub> Se	melt+HP	133	100	-48	1416	79
Cu <sub>2</sub> CdSnSe <sub>4</sub>	Cu <sub>2</sub> CdSnSe <sub>4</sub>	BM+SPS	252	-26	-33	182	76
PbS	Cu	ST+SPS	1177	-33	-8	400	80
Cu <sub>1.8</sub> S	Ru	BM+SPS	-24	20	-45	100	72
PbS	Sn	ST+HP	300	-19	11	122	42
SrNb <sub>0.15</sub> Ti <sub>0.85</sub> O <sub>3</sub>	Y-ZrO <sub>2</sub>	HP	73	-14	-16	877	81
(Ti,Zr,Hf)(Co,Ni)Sb	InSb	melt+SPS	-9	53	-21	150	6
Ti(Co,Fe)Sb	InSb	melt+SPS	115	48	-14	478	3
CuI	MXene	ST+HP	425	-62	-34	336	82

dispersed nanoinclusions have more significant reinforcement and strengthening properties.<sup>57</sup> However, the sintering temperature plays a crucial role in distributing the nanoinclusions such as inclusion growth, clustering, or fine dispersion; therefore, controlling the sintering time, temperature, and rate signifies the distribution of the nanoinclusions.<sup>24,65,66</sup>

Carrier Transport and Lattice Coherency. Carrier transport characteristics of nanoinclusions play a critical role as the compositing material's effective electrical conductivity (or effective  $\kappa$ ) increases if the nanoinclusion has a higher electrical conductivity (or  $\kappa$ ) than that of the matrix.<sup>67</sup> In the case of structural similarity between matrix and nanoinclusions phases, it helps to form a coherent interface, which enhances their charge carrier transport.<sup>68</sup> Generally, the coherent or semicoherent boundary forms during in situ formation such as precipitation.<sup>16</sup> For example, Xie et al.<sup>69</sup> added Si nanoinclusions to CoSi<sub>2</sub> due to their structural similarity, developing coherent interfaces and improving  $\sigma$ . Thus, nanoinclusions exhibiting a coherent interface with the matrix demonstrate an improvement or negotiable effect on electrical properties than do noncoherent boundaries that still impede phonons effectively.<sup>16,70</sup>

**Physical Stability of Nanoinclusion.** The nanoinclusions' mechanical, thermal, and phase stabilities are crucial, as they strongly influence the composite stability. The nanoinclusions should be stable; that is, they neither dissolute nor melt down during high-temperature service applications.<sup>71</sup> For example, Zhang et al.<sup>72</sup> added Ru metallic nanoinclusions to

the  $Cu_{1.8}S$  matrix, which strongly enhances the mechanical and thermal stabilities of the composite. The primary purpose of adding nanoinclusions in terms of mechanical strength is to act as obstacles to the dislocation motion.<sup>16</sup> The primary mechanisms of improving the mechanical properties by adding nanoinclusions are fine-boundary hardening and dispersion strengthening.<sup>13,33,73</sup>

#### METHODS OF NANOCOMPOSITE SYNTHESIS

During the synthesis of thermoelectric composites, nanoinclusions are added to the in situ and ex situ methods. In the in situ method, nanoinclusions are formed employing precipitation and spinodal or metastable phase decomposition, and in the ex situ method, nanoinclusions are added externally during the synthesis stage.<sup>5</sup> In situ formation of nanoinclusions with coherent boundaries leads to enhanced electrical properties in the material.<sup>9</sup> Hong et al.<sup>74</sup> determined that in situ formed inclusions, for example, superlattice precipitates, significantly enhance phonon scattering and then aid in achieving an ultralow lattice thermal conductivity. However, ex situ nanoinclusions are practical in creating reasonable control over the interfaces; therefore, the possibility of effectively decreasing  $\kappa$  is higher than in the in situ separated phase.<sup>75</sup> The ex situ method is advantageous over the in situ method as in facile synthesis, where it does not affect the stoichiometry of the matrix.<sup>76</sup> In situ nanoinclusions are formed during the spinodal decomposition of the metastable matrix phase or when precipitated out during nucleation and growth; therefore, these nanoinclusions create coherent or semicoherent interfaces with the matrix phase and result in a reasonable charge transport path.<sup>71</sup> However, ex situ nanoinclusions formation has a more powerful influence on reducing  $\kappa$  through phonon scattering than do in situ particles.



Figure 6. Increasing order of electrical conductivities of various carbon allotropes along with atomic structures.



Figure 7. (a) FESEM micrograph; (b) FETEM micrograph; and (c) elemental mapping of the  $SnS_2/MWCNT$  composite. Reprinted with permission from ref 94. Copyright 2022 American Chemical Society. (d) Hardness; (e) TGA; (f) electrical resistivity; (g) Seebeck coefficient; (h) thermal conductivity; and (i) *ZT* of carbon black nanoinclusions added to the  $Cu_3SbS_4$  composite. Reprinted with permission from ref 73. Copyright 2022 Elsevier.

Solid-state synthesis such as mechanical alloying, solution processes such as hydrothermal or solvothermal synthesis, and melting-based syntheses such as induction or arc melting are various synthesis routes used for nanocompositing. In most cases, thermoelectric nanocomposite materials are synthesized through either mechanical alloying or hydrothermal/solvothermal synthesis, followed by compaction sintering (i.e., spark plasma sintering or hot pressing), as shown in Figure 5. Melting is not widespread due to the significant difference in melting and boiling points between the elements in many thermoelectric compounds (for example, Pb, Se, S, Sn, and Sb have low evaporation temperatures).

#### CLASSIFICATION OF NANOINCLUSIONS

We classified the nanoinclusions into five types: carbon allotropes, secondary thermoelectric phases, metallic nanoparticles, oxides, and others (InSb, SiC, etc.), to produce a thermoelectric composite structure. Table 1 represents a few examples of the enormously improved thermoelectric performance (ZT > 100%) of the matrix-inclusion composite systems at their highest applicable temperatures. Figure 1b shows the number of articles published on these classified nanoinclusions based on thermoelectric composites in the year 2021. It suggests that researchers are showing more interest in carbon allotropic nanoinclusions-associated thermoelectric composites.

Carbon Allotropic Nanoinclusions. Carbon allotropes are mostly used and are well-established nanoinclusions for thermoelectric composite materials. Carbon is commercially available, lightweight, inexpensive, and has excellent semiconductive properties to add as a nanoinclusion to improve thermoelectricity. Carbon allotropes such as fullerene,<sup>52,83-86</sup> carbon black,<sup>73,87,88</sup> carbon fiber,<sup>89</sup> graphite,<sup>90</sup> carbon nano-tubes,<sup>46,91–94</sup> and graphene<sup>62,77,78,95,96</sup> are used as nanoinclusions to improve thermoelectric performance. Generally, carbon-based nanoinclusions are added to tailor both the electrical and the thermal properties due to the high concentration of charge carriers associated with them.8 Nandihalli et al.97 and Prunet et al.98 comprehensively explained that carbon allotropes are quite famous for acting as conductive nanoinclusions in polymer thermoelectric nanocomposites. Figure 6 shows the increasing order of electrical conductivities of different carbon allotropes and that graphene has the highest electrical conductivity of other



**Figure 8.** (a) TEM bright-field micrograph; (b) HRTEM micrograph; and (c) STEM elemental mapping of the PbTe/Cu<sub>2</sub>Se composite. Reprinted with permission from ref 79. Copyright 2016 IOP Publishing. (d) Strain distribution in the  $Mg_2Sn/Mg_3Sb_2$  composite. Reprinted with permission from ref 118. Copyright 2021 American Chemical Society. (e) Specific heat of the  $Ag_2Se/Cu_2Se$  composite. Reprinted with permission from ref 45. Copyright 2019 Elsevier. (f) Electrical conductivity; (g) Seebeck coefficient; (h) thermal conductivity; and (i) ZT of the  $Cu_2SnSe_3/Ag_2Se$  composite. Reprinted with permission from ref 112. Copyright 2022 American Chemical Society.

carbon structures. However, the observed increased carrier concentration reduces the  $\alpha$  in the carbon-based nano-composite. <sup>87,88</sup>

In many cases, due to the high reactivity of carbon, they react with one of the elements in the matrix and form secondary phases such as SiC<sup>52</sup> and ZrC.<sup>85</sup> Also, in some cases, during the addition of graphene nanoinclusions, graphite formations occur at grain boundaries via agglomeration during sintering.<sup>78</sup> These secondary phases are detrimental concerning their thermoelectric performance; therefore, nanoinclusions should be chemically inert with the matrix phase.<sup>52,85</sup> Carbon allotropes are also famous for their use in cement and organic thermoelectric composites to improve electrical transport.<sup>99</sup>

Fullerene was added to the thermoelectric matrixes such as skutterudite, half-Heusler, and Si-Ge compounds. Apart from reducing  $\kappa$ , fullerene maintains the  $\sigma$  with a lower reduction percentage because scattered electrons are compensated by fullerene carriers.<sup>52,83</sup> As compared to the fullerene molecule size, the electrical carrier's wavelength is large; therefore, it is ineffective for scattering charge carriers.<sup>84</sup> In the case of carbon black, an amorphous structure and cheap form of carbon allotropes are to be used as nanoinclusions.<sup>73</sup> The thermoelectric performance and mechanical stability of Cu<sub>3</sub>SbS<sub>4</sub> were strongly enhanced by adding carbon black nanoinclusions, as shown in Figure 7d-i.<sup>73</sup> Hossain et al.<sup>89</sup> added carbon fiber to the CoSb<sub>3</sub> matrix and observed a substantial increase in the electrical and thermal conductivity due to carbon atom doping. It is also reported that adding graphite nanoinclusions to the bismuth telluride increases  $\sigma$ , decreases  $\kappa$ , and improves the S simultaneously.<sup>90</sup> The large specific surface area associated with graphite structures is one of the primary reasons for the significant reduction in the lattice thermal conductivity.<sup>62</sup> The

effect of adding MWCNT nanoinclusions in the SnS<sub>2</sub> composite and their uniform distribution was confirmed by FESEM, FETEM, and EDS mapping, as shown in Figure 7a-c, a low amount of 0.5 wt % MWCNT causes an increase in the carrier concentration, and  $\alpha$  by reduced mobility was observed with reduced  $\kappa$  from phonon scattering in the skutterudite composite.<sup>46</sup> However, the agglomeration problems were encountered with more MWCNT, resulting in a decrease in  $\sigma$ .<sup>46</sup> Chen et al.<sup>100</sup> added MWCNT nanoinclusions in Ag<sub>2</sub>Se and observed an increase in  $\sigma$  and a reduction in  $\alpha$  and  $\kappa$ . Superior properties associated with graphene improve the  $\sigma$  to multiple folds by its high carrier concentration and mobility in the nanocomposite, enhancing thermal resistivity.<sup>77</sup> Because of a high specific area, its reduced densification creates pores and nanograin boundaries in graphene nanoinclusions, as reported in BiSbTe, showing a reduction in  $\sigma$  through a low carrier mobility.6

Secondary Thermoelectric Nanoinclusions. Thermoelectric phases added as nanoinclusions directly affect the *PF* on the basis of their carrier properties and the matrix phase; however, they reduce  $\kappa$ . Various thermoelectric phases such as  $CoSb_{3}^{10,51,57,101}$  PbTe,<sup>17,64,102</sup> ZnTe,<sup>103</sup> SnTe,<sup>104</sup> MnTe,<sup>105</sup> ZnSb,<sup>106</sup> Cu<sub>2</sub>CdSnSe<sub>4</sub>,<sup>76</sup> PbS,<sup>107</sup> Cu<sub>2</sub>Se,<sup>45,79,108</sup> Cu<sub>2</sub>Te,<sup>109</sup> Ag<sub>2</sub>Te,<sup>110,111</sup> Ag<sub>2</sub>Se,<sup>112</sup> FeSb<sub>2</sub>,<sup>113</sup> MoSi<sub>2</sub>,<sup>7</sup> MoS<sub>2</sub>,<sup>44,114</sup> full-Heusler,<sup>68,115</sup> Bi<sub>2</sub>Te<sub>3</sub>,<sup>116</sup> CuInTe<sub>2</sub>,<sup>117</sup> Mg<sub>3</sub>Sb<sub>2</sub>,<sup>118</sup> and Bi<sub>2</sub>Se<sub>3</sub><sup>119</sup> are used as nanoinclusions. Generally, these secondary thermoelectric-based nanoinclusions are mostly added through the in situ precipitation method.<sup>4,76,119</sup> Secondary thermoelectric nanoinclusions with a higher efficiency than the matrix phase are preferred to retain or increase electrical properties and reduce  $\kappa$ .<sup>7</sup> The selection of the thermoelectric nanoinclusions should be made to increase the *PF* along with reducing  $\kappa$ . Theoretical calculations on the half-Heusler matrix



Figure 9. (a) SEM micrograph and (b) corresponding elemental mapping of the Yb<sub>14</sub>MnSb<sub>11</sub>/W composite. Reprinted with permission from ref 126. Copyright 2019 AIP Publishing. (c) Change in electrical resistance and (d) hardness increased by Ru nanoinclusions in the Cu<sub>1.8</sub>S composite. Reprinted with permission from ref 72. Copyright 2021 Elsevier. (e) Electrical resistivity; (f) Seebeck coefficient; (g) thermal conductivity; and (h) *ZT* of the Cu/Fe nanoinclusions added to the SrTiO<sub>3</sub> composite.<sup>58</sup>

with skutterudite nanoinclusions report almost a 700% ZT enhancement.<sup>51</sup> In a half-Heusler matrix with full-Heusler nanoinclusions,  $\alpha$  and  $\sigma$  are enhanced at high temperatures because of coherency interfaces and obvious  $\kappa$  reduction.<sup>115</sup>

Thermoelectric nanoinclusion phases are not as stable as oxide nanoinclusions; sometimes, atoms diffuse into the matrix phase during heat treatment and contribute to the doping effect.<sup>119</sup> The addition of SnTe reduces the  $\sigma$ , not much change was observed in the  $\alpha$  in the SnSe matrix, and the overall effect on ZT was negligible.<sup>104</sup> An increase in  $\sigma$  by an increase in carrier concentration causes  $\alpha$  reduction and reduction of  $\kappa$  by phonon scattering and inhibition of the bipolar effect as observed in the SnSe matrix-PbTe inclusion combination system.<sup>102</sup> The addition of the semiconductor ZnTe inclusions improves  $\sigma$  by compromising  $\alpha$  as ZnTe intrinsically has a low  $\alpha$ . However, overall, ZT increased by 40% by providing a low  $\kappa$  in copper chalcogenide.<sup>103</sup> At the same time, the development of a high electrical resistivity and thermal conductivity by ZnSb in  $\beta$ -Zn<sub>4</sub>Sb<sub>3</sub> shows negative results.<sup>106</sup>

Interestingly, by increasing the Cu<sub>2</sub>Se nanoinclusions' concentration in the PbTe matrix, the system transforms from p-type to n-type due to the additional donor levels introduced by the antisite defects and unsaturated bonds at the interfaces.<sup>79</sup> Figure 8a–c shows the TEM micrographs with a clear contrast difference, atomic ordering, and elemental mapping of Cu<sub>2</sub>Se nanoinclusions in the PbTe matrix.<sup>79</sup> In situ precipitated Ag<sub>2</sub>Te formed simultaneously decouples the inter-relations between the thermoelectric parameters in the AgSbTe<sub>2</sub> composite.<sup>110</sup> However, extrinsically added Ag<sub>2</sub>Te nanoinclusions in the BST matrix reduce the  $\alpha$  due to the enormous  $\sigma$  increment from the carrier concentration and bipolar diffusion; however, *ZT* enhancement is observed.<sup>111</sup> As

shown in Figure 8d, adding Mg<sub>3</sub>Sb<sub>2</sub> nanoinclusions in the Mg<sub>2</sub>Sn matrix generates strain fields (dislocations) around inclusions and results in solid scattering points for both midand high-frequency phonons.<sup>118</sup> From the addition of MnTe to bismuth telluride, Mn atoms doped into bismuth lattice, enhancing the  $\sigma$  and reducing the  $\alpha$ .<sup>105</sup> A lower carrier concentration in the CoSb3 than the Yb0.15Co4Sb12 matrix reduced the overall carrier concentration of the composite.<sup>101</sup> The  $\sigma$  increased and the  $\alpha$  decreased with the addition of the Cu<sub>2</sub>Se nanoinclusion, likely due to the augmented carrier concentration in Ag<sub>2</sub>Se.<sup>45</sup> As shown in Figure 8e, the thermal stability of Ag<sub>2</sub>Se was also improved by the Cu<sub>2</sub>Se nanoinclusion. Ag<sub>2</sub>Se nanoinclusions in the Cu<sub>1.85</sub>Ag<sub>0.15</sub>Sn<sub>0.91</sub>In<sub>0.09</sub>Se<sub>3</sub> phase improve the Ag solubility and form the CuSe phase at grain boundaries; overall, this results in a  $\sigma$  decrease,  $\alpha$  increase,  $\kappa$  decrease, and overall improved ZT, as shown in Figure 8f-i.

Metallic Nanoinclusions. Metallic materials are known for high  $\sigma$  and  $\kappa$  values; therefore, adding metallic nanoinclusions in thermoelectric materials enhances  $\sigma$  significantly but also improves  $\kappa$ . Therefore, on the basis of the requirement to improve the  $\sigma$  of the nanocomposites, it is better to add metallic inclusions than other types (semiconducting or oxide) of nanoinclusions. The high carrier concentration associated with the metallic nanoinclusions nullifies the energy filtering effect to improve  $\alpha$  in some cases, which also depends on the matrix. The combination of high  $\alpha$  matrix and metallic nanoinclusions that provide phonon scattering and extra charge carriers is a good choice for a high ZT composite.<sup>42</sup> Mori et al.<sup>120</sup> suggested that this hybrid metallic web percolation scheme (which allows hybrid doping and composite effects) should be valid only for a high Seebeck coefficient, optimum electrical conductivity matrix, and



**Figure 10.** (a) Change in thermoelectric parameters by the oxide nanoinclusions. (b) TEM micrograph of  $Y_2O_3$  added to the BST matrix with the inset showing the SAED pattern. Reprinted with permission from ref 13. Copyright 2017 Elsevier. (c) The decomposition rate of  $Zn_4Sb_3$  changes by TiO<sub>2</sub> nanoinclusions. Reprinted with permission from ref 140. Copyright 2021 American Chemical Society. (d) Hardness improvement in BST matrix by  $ZrO_2$  nanoinclusions.<sup>33</sup> (e) Electrical resistivity; (f) Seebeck coefficient; (g) thermal conductivity; and (h) *ZT* of the TiO<sub>2</sub> nanoinclusions added to the Ba<sub>8</sub>Ga<sub>16</sub>Ge<sub>60</sub> composite. Reprinted with permission from ref 136. Copyright 2012 AIP Publishing.

relatively refractory metallic nanoinclusions. Generally, apart from the  $\kappa$  reduction by the addition of metallic nanoinclusions, the  $\sigma$  of the composite increases because of the high carrier concentration and high mobility attributions, which dominated the  $\alpha$  reduction from the increased mobility and increased carriers, implying a low filtering effect.<sup>34,58,106,121,12</sup> Therefore, the overall impact on the PF is completely based on the dominance phenomenon between  $\sigma$  and  $\alpha$ . Zianni et al.<sup>123</sup> suggested that in metallic nanoinclusions added to TE materials, the enhancement in Seebeck coefficient and electrical conductivity comes from the synergy between defects, charge neutrality, and energy filtering, which is possible after thermal annealing. Metallic nanoinclusions are added to improve  $\sigma$  by increasing the carrier concentration. Still, metal nanoinclusions sometimes improve the composite  $\kappa$ because of their high  $\kappa$ , especially copper.<sup>42,58</sup> Adding particles should be nonreactive or insulating with the matrix; otherwise, they act as dopants or form intermetallics.<sup>124</sup> The size and shape of the metallic nanoinclusions affect the energy filtering effect.<sup>125</sup> The composite's enhanced  $\kappa$  is due to the electron thermal conductivity contribution from the metallic nano-inclusions.  $^{58,106,121,126}$  Metallic inclusions such as Cu,  $^{42,58,80}$  Fe,  $^{58,121}$  Zn,  $^{106,127}$  B,  $^{124}$  Pt,  $^{128}$  Ag,  $^{24,49,66,125,129}$  Bi,  $^{34,122}$  Au,  $^{130}$  W,  $^{126}$  Si,  $^{47,69,131}$  Sn,  $^{42}$  Ge,  $^{132}$  Yb,  $^{133}$  Te,  $^{22}$  and In $^{70,75}$  were used to improve the thermoelectric properties.

The SEM micrograph of the Yb<sub>14</sub>MnSb<sub>11</sub>/W composite and the homogeneous distribution of W nanoinclusions are shown in Figure 9a and b. Srivastava et al.<sup>58</sup> demonstrated that Fe nanoinclusions exhibit a higher  $\alpha$  and lower  $\sigma$  than do Cu nanoinclusions in the SrTiO<sub>3</sub>-based composite because Fe has a lower  $\sigma$  than does Cu, as shown in Figure 9e and f. However, both Cu and Fe nanoinclusions enhance the total thermal conductivity of the composite due to the high thermal

conductivity of both of the metals and still improve the overall ZT of the composites, as shown in Figure 9g and h. Li et al.<sup>80</sup> added Cu metallic nanoinclusions to the PbS matrix, Cu dissoluted and formed Pb domains, and Cu<sub>x</sub>S precipitates improved the ZT. The addition of Ag/Cu nanoparticles in the TE matrix material enormously improved the carrier concentration, employing spontaneous doping of the Ag/Cu atoms.<sup>20</sup> A high  $\sigma$  associated with the silver and a vital electrical contribution to  $\kappa$  then enhanced the thermoelectric parameters.<sup>49</sup> That Zn nanoinclusions precipitated out from the matrix Zn<sub>4</sub>Sb<sub>3</sub> during processing due to the narrow phase transition for the  $\beta$  phase are proved with image analysis and lead to a reduction in  $\kappa$ .<sup>127</sup> Ullah et al.<sup>134</sup> added the Ag inclusions into the Al<sub>2</sub>O<sub>3</sub> oxide film, intending to improve the  $\sigma$  of the oxide phase. As shown in Figure 9c and d, adding Ru nanoinclusions in the Cu<sub>1.8</sub>S matrix enhances the temperaturedependent electrical and mechanical stability.<sup>72</sup> By adding Si to bismuth telluride, we observed that Si inclusion almost acts like oxide nanoinclusion.<sup>13</sup>

**Oxide Nanoinclusions.** Oxide nanoinclusions are chemically inert, facile, and low-cost approaches to responsibly enhance the thermoelectric efficiency.<sup>135</sup> Oxides typically have a wide bandgap or low  $\sigma$ , which are not significantly beneficial to add as nanoinclusions until they are only required to improve the *PF*.<sup>4</sup> However, oxide nanoinclusions help improve the thermal and phase stability, lowering  $\kappa$ , enhancing the mechanical properties, and improving the host's oxidation resistance; therefore, oxide nanoinclusions can add to any thermoelectric materials for controlled enhancement of *ZT*.<sup>4,81</sup> It is observed that oxides significantly enhance  $\alpha$  by energy filtering and reducing  $\kappa$  by phonon scattering, as shown in Figure 10a. Phonon scattering and electrical conductivity reduction contributed to the reduction in the overall  $\kappa$ .<sup>136</sup> For

example, nondiffusive ceramic oxides enhance the thermal stability in structurally unstable thermoelectric alloys such as Zn<sub>3</sub>Sb<sub>4</sub>, as shown in Figure 10c.<sup>137</sup> Oxides are also famous for enhancing the mechanical stability, as shown in Figure 10d. Oxides are commonly added as ex situ nanoinclusions during mechanical alloying.<sup>63</sup> Forming oxides in situ during synthesis is almost impossible because synthesis is carried out under a vacuum or argon atmosphere; if not, the matrix phase is affected. Rigid, thermally, and electrically impermeable inclusions such as oxide nanoinclusions have a maximum effect on the thermal and electrical carriers and enhance the mechanical stability.<sup>67</sup> There are various oxide-based nano-inclusions such as  $\text{TiO}_{2,}^{28,136-140}$  WO<sub>3,</sub><sup>29,141,142</sup>  $\text{ZrO}_{2,}^{23,27,33,55,56,81,143,144}$  Al<sub>2</sub>O<sub>3</sub>,<sup>31,145-147</sup> CeO<sub>2</sub>,<sup>63,148</sup>  $\text{Y}_{2}\text{O}_{3,}^{13,149}$  SiO<sub>2</sub>,<sup>135,150,151</sup> ZnO,<sup>30,64,137,152,153</sup> SrTiO<sub>3</sub>,<sup>61</sup> SnO<sub>2</sub>,<sup>154</sup> Yb<sub>2</sub>O<sub>3</sub>,<sup>60</sup> NiO,<sup>155</sup> and reduced graphene oxide<sup>156</sup> to improve the thermoelectric performance of the composites. Here,  $\alpha$  is expressed as  $\alpha = \gamma - \ln(n)$ , where  $\gamma$  is the scattering factor and *n* is the carrier concentration; 150 after the addition of oxide nanoinclusions,  $\gamma$  enhances and n decreases to increase the  $\alpha$  in two ways. However, adding a high concentration of oxide nanoinclusions reduces the  $\alpha$  due to that the scattering of a wide energy range of electrons eliminates the filtering effect.28

Reduction of  $\alpha$  in yttria dispersoids added to FeSi<sub>2</sub> by the dissolution of Y in the matrix increased the carrier concentration and depleted the common energy filtering effect.<sup>149</sup> Figure 10a shows the TEM micrograph with a clear contrast difference between the Y2O3 particles in the BST matrix.<sup>13</sup> The addition of 10 wt % WO<sub>3</sub> to a half-Heusler matrix showed electrical and thermal transport enhancement due to that the interaction of the nanoinclusions with the matrix forms a semiconducting or metallic character secondary phase (Zr, Hf)<sub>x</sub>WO<sub>3</sub>.<sup>142</sup> YSZ nanoinclusions with a high surface activation promote matrix grain growth, improving the carrier density and mobility.<sup>81</sup> ZrO<sub>2</sub> is selected over other oxide inclusions because of the lowest  $\kappa$ .<sup>56</sup> As shown in Figure 10e-h, the addition of oxide  $(TiO_2)$  nanoinclusions reduced the  $\sigma$  and  $\kappa$  and enhanced the  $\alpha$  of the composite (Ba<sub>6</sub>Ga<sub>16</sub>Ge<sub>30</sub>).<sup>136</sup> Suppose that by adding a high concentration of  $(CeO_2)$  nanoinclusions, the percolation network frame formations are observed, suppressing their mechanical stability.<sup>148</sup> Surprisingly, by adding optimal SiO<sub>2</sub> to an oxide  $(Ca_3Co_4O_9)$  thermoelectric composite,  $\sigma$  increases by the attributions from the generated point defects and enhanced carrier concentration.<sup>151</sup> NaCo<sub>2</sub>O<sub>4</sub> is one of the oxide-based nanoinclusions with high  $\sigma$  and  $\alpha$ , resulting in *PF* improvement and  $\kappa$  reduction.<sup>4</sup> NaCo<sub>2</sub>O<sub>4</sub> is the only studied nanoinclusion from an oxide family that enhances the PF, that is, a simultaneous improvement on each thermoelectric parameter. After NaCo2O4, researchers started exploring complex or layered oxide to improve the efficiency through simultaneous improvement in all three parameters.<sup>4</sup> There are no reports on enhancing three inter-related properties ( $\alpha$ ,  $\sigma$ , and  $1/\kappa$ ) simultaneously in the nanocomposite by adding oxide-based nanoinclusions other than NaCo<sub>2</sub>O<sub>4</sub>. Especially in improving the  $\alpha$  and reducing the  $\kappa$ , oxide (insulator)-based nanoinclusion dispersion is one of the better choices for the thermoelectric matrix.33

**Other Nanoinclusions.** Other nanoinclusions such as SiC,  $^{11,12,32,40,43,146,157-162}$  InSb,  $^{3,6,48,163-166}$  MXenes,  $^{82,167}$  BN,  $^{168}$  and TiB<sub>2</sub><sup>41</sup> are used in thermoelectric composites.

**Silicon Carbide.** SiC nanoinclusions reduce  $\kappa$  and enhance  $\alpha$ , but their  $\sigma$  depends on the matrix and the concentration of the inclusions. Adding SiC nanoinclusions, a semiconductor with a bandgap of 3.25 eV, the  $\sigma$  of the composite may increase<sup>160,162</sup> or decrease<sup>32,157</sup> depending on the matrix carrier density and the concentration of SiC. Generally, SiC increases the density of the defects such as antisite and point defects at interfaces, enhancing the carrier density.<sup>162</sup> The added SiC nanoinclusions in the NaCo<sub>2</sub>O matrix increase  $\sigma$ because of the increased defect concentration; therefore, all three thermoelectric parameters were improved simultaneously.<sup>12</sup> However,  $\alpha$  decreases by the addition of 1 vol % SiC because of the addition to oxygen contamination during the processing stage.<sup>32</sup> SiC added in whiskers and nanoinclusions form to synergistically enhance the mechanical stability by maintaining a ZT the same as the nanocomposite with SiC particles alone.<sup>159</sup> Adding SiC to  $Bi_2Sr_2Co_2O_y$  shows simultaneous enhancement of all three parameters.<sup>160</sup> The addition of coherent interfaced SiC nanoinclusions in the BiSbTe matrix improved all three thermoelectric parameters simultaneously.<sup>43</sup>

Indium Antimonite. Indium antimonite (InSb) is an intermetallic compound with a zinc-blend structure and shows strong semiconductive properties with a high carrier mobility and a narrow bandgap of 0.17 eV. InSb is one of the superior nonoxide-based inclusion types; adding InSb in composite simultaneously enhances the thermoelectric parameters, as observed in many cases. Simultaneous improvement of all three interconnected parameters by decoupling them by InSb is mainly because of the "electron crystal-phonon glass" phenomenon. InSb is one of the superior nanoinclusions, which shows better properties to improve the thermoelectric efficiency. Adding them both in situ and ex situ is reported; the carrier concentration is in the order of  $10^{17}$  cm<sup>-3</sup>, so it also contributes to  $\sigma$  by facilitating conductive channels across grains called carrier injection.<sup>163</sup> InSb nanoinclusions allow "carrier injection, energy filtering, and phonon scattering" mechanisms and create "electron crystal-phonon glass", as observed in thermoelectric composites.<sup>3,6,163,16</sup>

InSb is added as an ex situ nanoinclusion or formed in situ during the synthesis; however, in situ formed InSb nanoinclusions generally occur primarily on the grain boundaries.<sup>3,6</sup> Sometimes indium may react with atmospheric oxygen and form  $In_2O_3$ , which is detrimental in carrier scattering, increasing the electrical resistivity.<sup>164</sup> It improves the carrier concentration by showing semiconducting behavior with a narrow bandgap and reducing  $\kappa$  by employing phonon scattering centers by stable nanoinclusions and forming nanograin structures. Energy-based filtering or scattering around the nanoinclusions or nano boundaries is the primary factor in improving PF.<sup>6</sup> InSb improves the interlocked TE properties to increase the thermal efficiency by decoupling them. Decoupling is possible only up to a specific concentration of InSb; high concentrations increase the particle size, which is detrimental for carrier transport.<sup>6</sup> On inclusion with InSb in p-type tetrahedrite compounds, we observed a reduction in  $\sigma$  due to the formation of dangling bonds and antisite defects and common interfaces; however, simultaneous improvement in *PF* and  $\kappa$  was observed.<sup>165</sup>

High mobility electron injection increases the  $\sigma$  by employing a high carrier concentration, low energy electron filtering improves the  $\alpha$  by reducing the mean free path for low energy electrons, and boundary scattering of phonons reduces the  $\kappa$ <sup>3,6</sup> Despite increasing the number of grain boundaries by these InSb dispersoids, it shows a high  $\sigma$  because of the InSb semiconducting behavior and increased mobility. Generally, the  $\alpha$  increases with effective mass  $(m^*)$ , which implies a low carrier mobility, and phonon scattering substantially increases ZT,<sup>1</sup> which is observed in the InSb-added compounds. Because of the combination of "electron-filtering", "electron-injection", and "boundary phonon scattering" mechanisms, the interrelated  $\alpha$ ,  $\sigma$ , and  $\kappa$  are significantly decoupled, which will improve the TE parameters in both n-type and p-type semiconductors.<sup>3</sup> Simultaneous enhancement in inter-related thermoelectric properties of in situ InSb inclusion in half-Heusler compounds shows a ZT improvement of 160% and 450%.<sup>3,6</sup> Simultaneous improvement of TE parameters is possible only up to a particular concentration of InSb nanoinclusions; therefore, it is noteworthy that the percentage of improvement decreases when the typical size of nanoinclusions becomes larger with the InSb concentration.<sup>6</sup>

#### OUTLOOK AND CONCLUSIONS

The nanocomposite is a promising strategy to improve ZT by strongly reducing the lattice thermal conductivity. Nanoinclusions reduce the  $\kappa$  by employing interfacial boundaryassociated phonon scattering. The nanoinclusions' type, size effect, concentration, distribution, coherency, stability, and electrical and thermal conductivities are critical factors in enhancing the ZT of the material by forming a composite structure. Adding nanoinclusions improves the thermal, structural, and mechanical stability and the oxidation resistance. In nanocomposites, the combination of the mechanisms "energy-filtering", and/or "carrier-injection", or "carrier channeling" improves or maintains the PF, and "phonon scattering" reduces the  $\kappa$ , which all together helps in decoupling the inter-related  $\alpha$ ,  $\sigma$ , and  $\kappa$  consequently. As mentioned above, the composite structures significantly enhance the ZT by allowing at least two mechanisms. The nanocomposite is preferred to simultaneously improve all three interconnected parameters by decoupling through the "electron crystal-phonon glass" phenomenon, however, which is not observed frequently as the carrier concentration strongly contradicts  $\alpha$  and  $\sigma$  improvement.

The PF enhancement is difficult to estimate as it ultimately depends on the matrix and nanoinclusion electrical properties and the relative band alignments. We classified nanoinclusions into five types for the thermoelectric composite structures. Carbon allotropes are the most popular nanoinclusions for thermoelectric compositing due to their nonreactive, semiconducting properties and stability. These nanoinclusions improve the *PF* by improving  $\alpha$ ,  $\sigma$ , or both depending on the matrix. The effect of secondary thermoelectric nanoinclusions on PF solely depends on the type of nanoinclusion selected. However, secondary TE particles already have a good ZT, which positively influences all TE parameters of the composite. Metallic nanoinclusions are added to enhance the  $\sigma$ ; however,  $\kappa$  is also improved due to the high  $\kappa$  of the metals. Therefore, metallic nanoinclusions are specialized to increase the  $\sigma$  and *PF* of the matrix phase. Mechanically and thermally stable oxide-based nanoinclusions were added preferentially only to reduce  $\kappa$  and improve stability. However, the  $\alpha$ improves by reducing energy filtering and helps maintain PF. SiC is suitable for mechanical and thermal stability and enhancing PF. The  $\sigma$  increase by SiC nanoinclusions depends on the matrix electrical properties. Especially the addition of InSb nanoinclusions significantly affects ZT by improving the electrical conductivity, Seebeck coefficient, and thermal resistivity. Conclusively, we elucidate that the development of thermoelectric nanocomposites with semiconducting nanoinclusions is the best choice for a sustainable enhancement of power conversion efficiency in conventional thermoelectric materials.

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#### Notes

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