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Bulk Nanocomposites of Thermoelectric Materials

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3.1 Introduction

The phenomenon of thermoelectricity (TE), which was based on the Seebeck effect and the Peltier effect, was initially discovered in metals in the early 1800s. During the mid-twentieth century, with the discovery of semiconductors, the first-generation thermoelectric materials, such as Bi$_2$Te$_3$, PbTe, and SiGe, gave rise to commercial TE devices. However, wide application was obstructed by the low performance of the TE materials, since it was a great challenge to improve the $ZT$ value ($ZT = S^2T/\rho\kappa$, where $S$, $\rho$, $T$, and $\kappa$ are Seebeck coefficient, conductivity, absolute temperature, and thermal conductivity, respectively) above 1 in the following 50 years. Until the 1990s, the emerging of some new compounds, such as skutterudite and clathrate, brought great hope to overcome this problem. Besides that, nanotechnology has brought about a great change to the traditional TE materials. Various nanostructured materials, such as nanocomposites$^1$, superlattice$^{2,3}$, quantum well, and dots$^{4-6}$ have improved the $ZT$ values to 2, which arouses great enthusiasm among TE researchers. Figure 3.1 shows the history of development over the past 60 years.

Up to now, the nanostructured TE materials mainly include three kinds of materials, that is, low-dimensional materials, nanograin-sized materials, and nanocomposites. From the traditional view, thermoelectric materials are expected to be pure semiconductors without any secondary phase to avoid the impurity scattering to electrons. It has been proved that, by both theoretical predication and experimental results, the TE performance of large-scale composites is just a compromise of the two (or more) phases. However, with the progress of fabrication technique and microstructure characterization, when the second phase goes into nanosize, TE performance can be improved if the nanoinclusions scattering is applied to appropriately tuning the transport of electrons and phonons. And bulk nanocomposites, which contain nanoinclusions dispersing in the matrix, are expected to be one of the most potential thermoelectric materials for wide use in the future.
ZT improvements brought by nanocomposites have been confirmed in many TE systems. One typical example is PbTe, which was a traditional thermoelectric material in moderate temperature used by NASA in the 1960s. Doping was the main approach to optimize the thermoelectric performance for a long time, and $ZT \sim 0.8$ was obtained. In 2004, Kanatzidis et al.\(^1\) reported $\text{AgPb}_m\text{SbTe}_2\text{$_m$}$ nanocomposite containing $\text{Ag}^+\text{Sb}^{3+}$-rich nanodots, and the maximal $ZT \sim 2.2$ at 800 K was achieved. From then on, PbTe-based nanocomposites dispersing with PbS\(^7\) and Na-Sb\(^6\)-rich nanodots were fabricated, and found that the microstructure fluctuation contributes to the enhanced thermoelectric performance. Another example is the Bi\(_2\)Te\(_3\)-based alloy, which functions around room temperature. The thermoelectric performance of zone-melted Bi\(_2\)Te\(_3\) was around $ZT = 1$ in the earlier decades. Recently, Chen and Ren et al.\(^9\) reported nanostructure p-Bi\(_2\)Te\(_3\) with high $ZT$ value made by ball milling. It is concluded that the enhancement of $ZT$ originated from the greatly depressed lattice thermal conductivity. Tang and Tritt et al.\(^10\)\(^−\)\(^12\) fabricated nanostructure Bi\(_2\)Te\(_3\) by melt spinning. The contact face is nanograined or amorphous, and the free face grain is in microsize. Due to the micro–nano composite microstructure, the lattice thermal conductivity is obviously depressed, and the $ZT$ values are greatly improved to 1.56. In the following reports, skutterudites with nanostructures Yb\(_2\)O\(_3\),\(^13\) InSb,\(^14\) and GaSb\(^15\) are fabricated by different routes, and the $ZT$ value approaches 1.5, that is, about 25% enhancement comparing with $ZT \sim 1.2$ of the matrix.

In this chapter, we will introduce the recent developments of thermoelectric nanocomposites in various systems, including fabrication and microstructure analysis of nanoinclusions, the effect of nanoinclusions on the transport character and the mechanisms underlying. The investigations of microstructure stability in skutterudites are also discussed.

### 3.2 Fabricating Methods and the Microstructure of Nanocomposites

Up to now, semiconductors and insulators have been found to be suitable when choosing nano dispersions, because these compounds are inert to the matrix when the TE materials are subjected to high temperature. Some active metal elements and compounds with low melting point or high vapor pressure are usually excluded. The following factors would be considered when fabricating nanocomposites. (1) The grain size of nano dispersions is expected to be below 100 nm, for the mean free path of phonons is just about several nanometers. (2) Homogeneous distribution in the matrix of the nano dispersions is desired to scatter phonons on a large scale. (3) The integrality of the matrix, especially the electron transport channels, would not be destroyed by the introduction of nanodispersions. (4) The
thermodynamically stability of nanodispersions is also an important issue for the application of devices. The microstructure schematic of the nanocomposite is shown in Figure 3.2a. Nanoinclusions are dispersed homogeneously, not only locating at the grain boundaries, but also inside the grains.

For the above reasons, the fabrication of nanocomposites fulfilling the above-mentioned features integrates mechanical engineering, kinetics, phase diagrams, and some other materials sciences. According to the formation of the nanoinclusions, two major routes are applied to fabricate the thermoelectric nanocomposite: the \textit{ex situ} method, involving mechanical mixing$^{16,17}$ and liquid–solid compositing,$^{18,19}$ and the \textit{in situ} method, involving phase decompositions$^{20-24}$ and nanosize precipitations.$^{25-27}$

\subsection*{3.2.1 Ex Situ Route}

The first step of fabricating nanocomposites via the \textit{ex situ} route is to prepare the nanosized second particles, and then disperse them into bulk matrix materials by following the mixing and sintering process. The sketch map is shown in Figure 3.3. Initially, skutterudite-based nanocomposites were produced via high-energy ball milling, which is a typical \textit{ex situ} route. High-energy ball milling could produce large amounts of particles with a grain size as small as several nanometers. The nanosized second phase CoSb$_3$/FeSb$_2$,$^{28}$ CoSb$_3$/NiSb,$^{29}$ CoSb$_3$/C$_{60}$,$^{30}$ Ba$_{0.44-x}$Co$_4Sb$_{12}/Ba$_x$C$_{60}$,$^{31}$ and CoSb$_3$/ZrO$_2$,$^{32-33}$ were fabricated via this approach. Most nanodispersions are distributed in the grain boundaries while some are enclosed inside the grains during the sintering process.

Research conducted also included half-Heusler compounds, which have high thermal conductivity. Chen et al.$^{34}$ introduced nanoparticles ZrO$_2$ to the alloys Zr$_{0.5}$Hf$_{0.5}$Ni$_{0.8}$Pd$_{0.2}$Sn$_{0.99}$Sb$_{0.01}$. The microstructure analysis is shown in Figure 3.4.

Another \textit{ex situ} method, liquid–solid compositing, was applied as an effective \textit{ex situ} method to introduce nanodispersions in the matrix. During the period of hydroxylation, nanodispersions are precipitated on the surface of matrix particles, which will make a homogenous distribution of the nanodispersion in the matrix. And the size of nanoparticles could be more uniform compared to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{3.2.png}
\caption{Microstructure schematic of the nanocomposite. (a) Nanodispersions are homogeneously dispersed; (b) nanodispersions are gathered at the grain boundary.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{3.3.png}
\caption{Sketch map of the \textit{ex situ} compositing method.}
\end{figure}
the ball-milling process. In the series La$_{0.9}$CoFe$_3$Sb$_{12}$-CoSb$_3$, CoSb$_3$(micro)/CoSb$_3$(nano), and Ba$_{0.22}$Co$_4$Sb$_{12}$/TiO$_2$, nanodispersions were both introduced in the liquid circumstance. Microstructure of the Ba$_{0.22}$Co$_4$Sb$_{12}$/TiO$_2$ nanocomposite was shown in Figure 3.5.

### 3.2.2 In Situ Route

The *in situ* route is a way in which the nanosized particles form in the homogeneous matrix via nucleation and growth. The *in situ* route, which means at least one component of the nanodispersions come from the matrix, usually resulting in nanocomposites with a homogeneous microstructure. One typical *in situ* route is that nanophase is precipitated in the supersaturated matrix during the cooling process. The size of the second phase can be controlled by a certain heat-treatment process, and the distribution is greatly enhanced compared with the *ex situ* route. *In situ* oxidizing, nonuniform growth via melting, spinning, metastable voiding, and filling have been explored for skutterudites-based nanocomposites in recent years.

#### 3.2.2.1 In Situ Oxidization

In the process of fabricating thermoelectric compounds, some components are added in excess for the purpose of being oxidized in the following period, called *in situ* oxidation. *In situ* oxidation was used in the preparation of Yb$_2$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ nanocomposites. In the annealing period (1000–1100 K), the rare earth metal Yb has a higher filling fraction in the voids of CoSb$_3$ than that at room temperature. As the temperature is lowered, the *in situ* precipitated Yb is oxidized to Yb$_2$O$_3$. Some nanosized Yb$_2$O$_3$ are observed inside the matrix grain and some dispersion with micro size are located in the grain boundary as well. The sketch map and the microstructure are shown in Figures 3.6 and 3.7, respectively. The $\kappa_L$ was drastically depressed due to the existence of Yb$_2$O$_3$ nano-oxides and a $ZT$ of 1.3 was achieved.

In the preparation of half-Heusler compound TiFe$_{0.2}$Co$_{0.8}$Sb, L. D. Chen et al. have added trace oxidant Fe$_2$O$_3$ into the matrix. In the arc-melting process, excess Ti is oxidized into TiO$_2$ by oxidant Fe$_2$O$_3$ as the following reaction:

$$3\text{Ti} + 2\text{Fe}_2\text{O}_3 \rightarrow 3\text{TiO}_2 + 4\text{Fe}$$

The *in situ* oxidized TiO$_2$ nano-inclusions are dispersed in the TiFe$_{0.2}$Co$_{0.8}$Sb matrix, as shown in Figure 3.8.

#### 3.2.2.2 Nonuniform Growth

Melt-spinning is an ultrafast cooling technique, which is usually used to produce metal glass because the nucleation and growth of grains is prevented by the super-cooling. The grain in the contact face
FIGURE 3.5 TEM images for the nanocomposite Ba$_{0.22}$Co$_4$Sb$_{12}$/0.4vol.%TiO$_2$. (a) Composite powder. (b–d) Sintered bulk. The inset of (b) is the EDS results of the circled area.

FIGURE 3.6 Sketch map of *in situ* oxidization for Yb in Yb$_y$Co$_4$Sb$_{12}$. 

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is nanosized or amorphous, while the grain in the free face is microsized. This allows the nonuniform growth of the grains to be possible in the following SPS or hot press sintering process. The sketch map of melt spinning is shown in Figure 3.9. Tang et al.\textsuperscript{43} added excess Sb when fabricating Yb\textsubscript{x}Co\textsubscript{4}Sb\textsubscript{12}, and after melt-spinning, found that the excess Sb were locating on the grain boundaries. The $\kappa_L$ was observed to be depressed as other nanodispersion containing series. Tang and Tritt et al.\textsuperscript{11,12} prepared Bi\textsubscript{2}Te\textsubscript{3}-based nanocomposite by melt spinning, and found that nanograins were dispersed in the micro-sized matrix with coherent boundaries, which is helpful for reducing the lattice thermal conductivity while maintaining the electrical conductivity.

### 3.2.2.3 Precipitation from Metastable Phase

So far, a variety of atoms have been successfully filled into the voids of CoSb\textsubscript{13}-based skutterudites, such as rare earth elements, alkaline earth elements, and alkaline elements.\textsuperscript{44–46} When Chen and Zhang et al. studied the filling fraction of the available fillers, they found that some elements may fill into the void in a metastable state.\textsuperscript{15} They focused their attention on the IIIA elements, that is, Ga, In, and Tl, which
remain ambiguous in skutterudite systems.\textsuperscript{47,48} As shown in Figure 3.10, \textit{ab initio} calculations reveal that the $\Delta G$ of Ga-filled CoSb$_3$ turns to positive when the temperature is below 1100 K, which implies a possible metastable void filling in CoSb$_3$. This suggests a precipitation route to produce nanocomposite, that is, filling Ga into the void at high temperature and driving it out when the temperature is lowered, forming related nano-inclusions in an \textit{in situ} way.\textsuperscript{22,26} The sketch map is shown in Figure 3.11. A TEM image of the quenched sample (Figure 3.12) Yb$_{0.26}$Ga$_{0.24}$Co$_4$Sb$_{12.2}$-q combining with the EDS results shows a homogeneous microstructure, which proves that Ga filling to the CoSb$_3$ voids at high temperature. For a furnace cooling procedure, the metastable filling Ga was driven out of the voids and formed GaSb nano-inclusions in an \textit{in situ} way. As shown in Figure 3.13, GaSb nano-inclusions with grain size $\sim$11 nm are dispersed homogeneously in the nanocomposite Yb$_{0.26}$Co$_4$Sb$_{12}$/0.2GaSb. To control the grain size of nano-inclusions, the cooling procedure of the Ga–Yb dual filling samples at high temperature is adjusted, then the GaSb grain size is coarsened to $\sim$88 nm in the nanocomposite Yb$_{0.26}$Co$_4$Sb$_{12}$/0.2GaSb-c, as shown in Figure 3.14.

Samples of Yb$_{0.26}$Co$_4$Sb$_{12}$/yGaSb were fabricated and proved that the GaSb nanodispersion in the grain size of 5–20 nm are locating homogeneously in the matrix of Yb-filled CoSb$_3$. The Seebeck coefficients of GaSb containing samples were enhanced at the same carrier concentration level. As a result, the $ZT$ values are increased in the whole temperature range.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.9.png}
\caption{Sketch map of the melt-spinning method.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.10.png}
\caption{Predicted temperature-dependent Gibbs free energy $\Delta G$ in filled skutterudite Ga$_x$Co$_4$Sb$_{12}$.}
\end{figure}
3.3 Transport Characteristics for the Skutterudite-Based Nanocomposites

For the state-of-the-art TE materials, wavelength ($\lambda$) and mean free path ($l$) are two critical factors for both electron and phonon transport. In a Boltzmann approximation, the lattice thermal conductivity and carrier mobility are in proportion to the mean free path of phonons ($l_{ph}$), and that of carrier ($l_e$), accordingly. Based on the scattering theory, the waves will be scattered strongly by the objective possessing the equivalent size as the wavelength. For an electron, $\lambda_e$ and $l_e$ occur in the scale of nanometers, while those of a phonon ($\lambda_{ph}$ and $l_{ph}$) distribute in a broader range. The difference of $\lambda_e$ and $\lambda_{ph}$ make it possible to selective scattering brought by the suitable-sized nanoparticles, which would effectively reduce $l_{ph}$ but not $l_e$.49–53 Usually, comparing with the pure thermoelectric matrix, three changes in
thermoelectric properties are expected for the nanocomposites. (1) The $\kappa_L$ is decreased due to the scattering effects to phonons from the scattering centers both of nanoinclusion and the interface. 49,54–56 (2) The Seebeck coefficient is expected to increase by a degree, which may be attributed from the filtering effects to electrons of low energy, resulting in the increasing change of carrier DOS dependent on energy near the Fermi level. 51,57,58 (3) The electrical conductivity may be influenced, depending on the characteristic of the nanodispersions. The Hall mobility may be affected for the nanoscattering to electrons. Nevertheless, the $ZT$ value could be enhanced if the microstructure is carefully manipulated to minimize the effect to mobility. Tremendous experiments have revealed the promising potential.

3.3.1 The Impact on Phonon Scattering and Thermal Conductivity

For unfilled skutterudites, the improvement of TE performance after compositing with nanoinclusions is considerable. The phonons have very large mean free path values without the “rattling” effects of
fillers to scatter phonons; therefore, once the scattering center such as nanoscale or larger-scale defects are introduced, the depression of the lattice thermal conductivity is prominent. For instance, $\kappa_L$ among the nanocomposite CoSb$_3$/6.54 wt.%C$_{60}$ has a factor of 2 smaller than that of the pure CoSb$_3$. And composites of CoSb$_3$/FeSb$_2$, CoSb$_3$/NiSb, CoSb$_3$/C$_{60}$, and CoSb$_3$/ZrO$_2$ were also fabricated to explore the large defect scattering effects to phonons. The improvement of $ZT$ is mainly attributed from the depression of $\kappa_L$.

For filled skutterudites, as the fillers could dramatically impede the transportation of phonons with short–middle wavelength, the nanoscattering mainly takes effect in long wavelength spectrum range. For instance, $\kappa_L$ of the nanocomposite Ba$_{0.22}$Co$_4$Sb$_{12}$/0.4vol.%TiO$_2$ decreases by 12% comparing with that of the matrix; however, $\kappa_L$ of the nanocomposite Ba$_{0.22}$Co$_4$Sb$_{12}$/1.8vol.%TiO$_2$ increases by 28%. As the interface effects turn to volume effects, the total $\kappa_L$ is a compromise of the matrix and the second phase. Since the nanodispersions, including oxides and semiconductors, have higher thermal conductivities than the filled skutterudite, the total $\kappa_L$ will increase once the nanodispersions exceed the optimal content.

Yb is effective in reducing the $\kappa_L$ due to its heavy element mass and small radius, but the presence of Yb$_2$O$_3$ can scatter the phonons more drastically. The $\kappa_L$ for the nanocomposite Yb$_{0.25}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ at room temperature is depressed to 1.72 W m$^{-1}$ K$^{-1}$ with the Lorentz number 2.0 E$^{-8}$V$^2$ K$^{-2}$. The $\kappa_L$ of some typical systems nanocomposites are displayed in Figure 3.15.

The scattering mechanism of nanoinclusion to phonon is complicated. Two aspects should be considered. The scattering comes from the nanoinclusion and from the interface. Interface is a discontinuous part in the nanocomposites, at which the elastic modulus, crystal plane matching, and Fermi level, and so on are all changed abruptly. During the transportation, phonons will be scattered at the

![FIGURE 3.14 FESEM images for fractured surface of the sample Yb$_{0.26}$Co$_4$Sb$_{12}$/0.2GaSb nanocomposite (a) and Yb$_{0.26}$Co$_4$Sb$_{12}$/0.2GaSb-c nanocomposite (c) with large GaSb dispersions. (b) and (d) are the corresponding grain size distribution for (a) and (c), respectively.](image-url)
interface due to the above reasons. The interface of inclusion and the matrix can be regarded as several phonon scattering centers. Regarding the phonons as particles during transport in the solid materials, it would be scattered strongly by the inclusions possessing the equivalent grain size, then the inclusion serves as phonon scattering centers. Comparing with point defects, which are in the atomic level, nanoinclusion mainly scatters the mid-to-long wavelength phonons, and then the lattice thermal conductivity.

### 3.3.2 The Effect on Electrical Transportation

The change of electrical conductivities is strongly dependent on the nature of nanodispersions. For n-type skutterudite nanocomposites, nanoinclusions of metal will increase the carrier concentration, and usually, the enhancement of electrical conductivity is difficult to offset the decrease of Seebeck and the increase of electron thermal conductivity. The insulator and semiconductor are usually chosen as the candidates for nano-inclusions due to their stable characteristics. Oxides, being inert to the matrix and only worked as phonon scattering centers, usually exert negative influence on the electrical conductivity. As the concentration exceeds the optimal content, in other words, the nano-dispersions are connected with each other and form a barrier layer in the grain boundary, the electrical conductivity will be depressed on a large scale. For filled skutterudites, the heavily doped semiconducting behavior will be changed to an intrinsic semiconducting pattern. The electrons have to cross the insulator layer for electrical conductivity to take place, which is strongly dependent on the temperature. Thus, for material design, the most important issue is to avoid aggregation of the second phase.

The dispersed inclusions can also scatter electrons in a degree, behaving as the mobility is lowered. For instance, the electron mobility of Ba$_{0.22}$Co$_{0.5}$Sb$_{1.2}$/TiO$_2$ nanocomposite is declined when compared with the matrix, which can also be found in the nanocomposites CoSb$_2$/C$_{60}$ and Yb$_{0.32}$Co$_{0.5}$Sb$_{1.2}$/GaSb. The electron–phonon scattering mode is dominant for skutterudites, nanocomposites also obey the $\mu_1 \sim T^{-3/2}$ relationship largely once the nano inclusion content is not high enough. The departure implies the change of scattering parameters as shown from the results of the nanocomposites Ba$_{0.22}$Co$_{0.5}$Sb$_{1.2}$/TiO$_2$ and CoSb$_2$/C$_{60}$ in Figure 3.16. Thus, what we could do is to control the content and distribution of the nanodispersions not to reduce the mobility much, at least, smaller than the beneficial effect for Seebeck coefficient.
At the interface of nanocomposites, a barrier is formed due to the different Fermi level between the nanoinclusion and the matrix. It is generally believed that such a barrier can filter electrons with low energy. As a result, the change of carrier density depending on energy near the Fermi level could be increased, which is helpful for enhancing the Seebeck coefficients. It is indeed that the absolute Seebeck coefficients are improved in the reported nanocomposites CoSb₃/C₆₀, InₓCe₁₋ₓCo₄Sb₁₂/InSb, and Ba₀.₂₂Co₄Sb₁₂/TiO₂. For the nanocomposite Yb₀.₂₆Co₄Sb₁₂/GaSb, the Seebeck coefficient is enhanced at the same carrier concentration, as shown in Figure 3.17.

For semiconductors with a single parabola band mode, the power factor (S²σ) usually has a parabola-like trend depending on the carrier concentration. It is indeed that the absolute Seebeck coefficients are improved in the reported nanocomposites CoSb₃/C₆₀, InₓCe₁₋ₓCo₄Sb₁₂/InSb, and Ba₀.₂₂Co₄Sb₁₂/TiO₂. For the nanocomposite Yb₀.₂₆Co₄Sb₁₂/GaSb, the Seebeck coefficient is enhanced at the same carrier concentration, as shown in Figure 3.17.

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FIGURE 3.16 (a) Temperature dependence of $\mu_H$ (hall mobility) for the nanocomposite Ba₀.₂₂Co₄Sb₁₂/TiO₂; (b) Arrhenius plot of ln($\mu_H T^{0.5}$) vs 1/(kᵦT) for the nanocomposite CoSb₃/C₆₀.
3.4 Microstructure Stability of Thermoelectric Nanocomposites

The application situation demands that TE materials should be able to function at a relatively high temperature for a long term. And the elements may also diffuse from a high concentration to a low concentration due to the temperature gradient. Therefore, the stability of the thermodynamics and microstructure is vital to the thermoelectric performance. Chen and Gu et al. \(^70\) focused on the microstructure stability of skutterudite nanocomposites \(\text{Yb}_x\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3\), in which nano-\(\text{Yb}_2\text{O}_3\) inclusions were proved to be effective phonon scattering centers. The composite \(\text{Yb}_{0.6}\text{Co}_4\text{Sb}_{12}/\text{Yb}_2\text{O}_3\) was heat treated at 600°C for a

![FIGURE 3.17](image1)

Seebeck coefficients of \(\text{Yb}_x\text{Co}_4\text{Sb}_{12}\) and \(\text{Yb}_{0.26}\text{Co}_4\text{Sb}_{12}/\text{yGaSb}\) virus carrier concentration. (Adapted from G. S. Nolas et al. 2000. *Appl. Phys. Lett.* 77, 1855; G. A. Lamberton et al. 2005. *J. Appl. Phys.* 97, 113715; Xiong Z, J. D. et al. unpublished.)

![FIGURE 3.18](image2)

FIGURE 3.19  Microstructure characterization of the Yb$_{0.6}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ samples. (a) Shows the back scattering image of the polished surface for the sample heat treated for 0 day. (b) The SEM image of the polished surface for the sample heat treated for 30 days. (c–d) Shows the TEM image for the sample heat treated for 30 days.

FIGURE 3.20  ZT values for the Yb$_{0.6}$Co$_4$Sb$_{12}$/Yb$_2$O$_3$ samples heat treated for 0, 10, 20, 30 days, respectively.
duration of 10, 20, and 30 days, respectively. The TEM images reveal that the microstructure of Yb<sub>0.6</sub>Co<sub>4</sub>Sb<sub>12</sub>/Yb<sub>2</sub>O<sub>3</sub> nanocomposite is stable even when the sample was heat treated at 600°C for 30 days. As shown in Figure 3.19c,d, dislocations are estimated to be the reason for microstructure stabilization. The stress induced by dislocation can prevent the filling Yb from diffusion. Figure 3.20 shows the ZT values for the Yb<sub>0.6</sub>Co<sub>4</sub>Sb<sub>12</sub>/Yb<sub>2</sub>O<sub>3</sub> nanocomposite heat treated for different duration. The results indicate that the ZT deviation is limited to be 10%.

3.5 Summary and Future

In the past decade, various nanocomposites with enhanced ZT values have been successfully produced, and nanostructuring has become a common strategy to improve the performance of TE materials. At present, most enhancements of TE performance are mainly attributed to the reductions of lattice thermal conductivity, and the comprehension that nanoinclusion effectively scattering the mid-to-long wavelength phonons has been confirmed. However, further improvement of ZT requires not only the decrease in thermal conductivity, but also the enhancement of power factor. Although theoretical studies by Dresselhaus et al.71,72 were impressive, however, researchers have realized that nanoinclusion could change the transport behavior of the carriers,15,69 the scattering mechanism is still very ambiguous, and it remains a great challenge to control the scattering process to improve the power factor.

Besides comprehensive problems of the mechanism, other challenges mainly are concentrated in how to fabricate nanocomposites with a desired microstructure, that is, homogeneous distribution of nanoinclusions with suitable size. Precipitation caused by thermokinetics is expected to be the ideal approach to realize that. However, the studies on the thermodynamics phase diagrams of TE systems seem to be insufficient. The related works would be very necessary and helpful for TE nanocomposites engineering in the future. In the development history of TE materials, the TE performance is approaching limitation before the nanostructuring concept. With the progress of theory and fabricating technology, we hope a ZT of 2 or even higher values could be realized in TE nanocomposites.

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