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# Thermoelectric Nanocomposites – A New Paradigm

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## Abstract

While the heavily doped narrow gap semiconducting bulk materials still remain the cornerstone for commercial applications in thermoelectric (TE) power generation and refrigeration, the TE nanocomposite materials attract lots of interest due to the great potential of improving the figure of merit  $ZT$ . Formed by either pure nanomaterial or by incorporating nanostructures into host bulk matrix material, the nanocomposites exhibit significantly reduced thermal conductivity due to the grain boundary scattering of phonon. Within the nano-constituent the band structure and transport of electron and phonon are significantly different from the bulk counterpart, which provides extra control of the structure-property correlation. As a result, the  $ZT$  can be improved in a scalable, cost effective way. In this paper we shall have a brief survey of the recent advance in fabrication and characterization of TE nanocomposites. The importance of the materials synthesis processes, interface effects and micro-morphology has been addressed.

*Dedicated to Prof. Terry M. Tritt on the occasion of his award of the SCAS Governor's Research Professor of Year 2008.*

**Keywords:** thermoelectrics, figure of merit, nanocomposites.

## 1. Introduction

Heat from various sources such as solar heat, geothermal heat and exhaustion of the automobiles can be directly converted into electricity using thermoelectric (TE) device (via the "Seebeck effect"). Reversely the TE device can work in a refrigeration mode (via the "Peltier effect"). Being all-solid assembly, responsive, moving-part free and easy to be coupled to other energy-conversion techniques, the TE device has found niche applications for deep space missions, as well as laboratory and medical equipments, where issues such as cost and efficiency are less important than that of overall energy reliability, the size of the device and quiet operation. [1]

In order to compete with those currently used commercial power generation and refrigeration technologies in efficiency, an improvement of a factor of 2-4 is needed in the performance of TE material, which is determined by the dimensionless figure of merit,  $ZT$ ,

$$ZT = \frac{\alpha^2 T}{\rho \kappa} = \frac{PF}{\kappa} = \frac{\alpha^2 T}{\rho(\kappa_l + \kappa_e)} \quad (1)$$

where  $\alpha$  is the Seebeck coefficient,  $\rho$  the electrical resistivity,  $\kappa$  the thermal conductivity (including the lattice thermal conductivity  $\kappa_l$  and carrier thermal conductivity  $\kappa_e$ ),  $PF$  the power factor, and  $T$  the temperature in Kelvin. Accordingly a good TE material should combine high Seebeck coefficient, low electrical resistivity and low thermal conductivity  $\kappa$ . The state-of-the-art TE materials have  $ZT \sim 1$  in their application temperature range. Further improvement of  $ZT$  is restricted by the fact that  $\alpha$ ,  $\rho$  and  $\kappa$  are inter-related: optimizing one often adversely affects the others.

Per equation (1), central to improving  $ZT$  is to manage the electrical and thermal energy transport in the material such that property-wise the material is a "Phonon-Glass Electron-Crystal" (PGEC) [2]. In complex crystal systems composed of building modules with different compositions, structural symmetries and TE functions, sometimes called "hybrid crystal", the electrical and thermal transport can be decoupled and optimized. The novel misfit-layered cobalt oxides [3], filled skutterudites [4, 5], and novel Zintl-phase [6, 7] compounds provide examples of such control.

Furthermore, it is important to recognize that a PGEC system is not necessarily a homogeneous system, the multiphase composite materials suppose to have greater flexibility and tunability. However, the composite approach is limited from the theoretical point of view. The effective medium approximation (EMA) model, the commonly used theoretical tool to analyze the transport property in composite, asserts that the conductivity property of a composite system can not exceed that of the best/worst performing constituent of the composite if there is no contribution from the interface/grain boundary [8].

In order to conduct a composite approach, the role of the interface/grain boundary must be addressed in the first place. When the characteristic length of one or more constituents in the composite is reduced to the nanometer level, the interface effect can be a dominant factor in light of  $10^{19}$  or more interfaces per  $\text{cm}^3$ . In general the interface/grain boundary provides an effective avenue to scatter phonon and subsequently lower the thermal conductivity, while the effect on the Seebeck coefficient is usually minor, but it is hard to do this without simultaneously degrading the electrical conductivity. There are several solutions. First, in some coarse-grain systems like half-Heusler compound, where the electrical conductivity is underlain by the number of carrier

more than the mobility, the grain boundary can scatter phonon more than electrons when the grain size is in a proper range [9]. Also, one can fabricate a thermoelectrically favorable grain boundary. In the hydrothermally treated  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$  fine-grain systems, the systems exhibited improved electrical-to-thermal conductivity ratio via grain boundary engineering [10, 11].

In addition to the interface/grain boundary effect, when the characteristic length of a constituent is below  $\sim 100$  nanometer, the band structure and transport mechanism of carrier and phonon in that nano-constituent are expected to be significantly different from those of the bulk counterpart due to the classic and quantum size effects. There are two different length scales, wavelength and mean free path, of electron and phonon affecting the electrical and thermal transport. In the case of phonon, the wavelength is important for estimating the confinement-induced dispersion relation change and the relative weight of diffusive vs. specular interface scattering; while the mean free path is important for estimating the mean free path reduction due to the grain boundary scattering. Similar argument applies to electron. As Heremans and Dresselhaus early pointed out, the reduced dimensionality and dimension brought about encouraging effects in the band structure and transport mechanism in the Te point of view [12]. As a result, the ZT of the nano-constituent can be higher than its bulk counterpart, consequently, the ZT of the composite can be improved (within the frame of EMA).

Though categorized as low dimensional system, the engineered superlattice system (ESS) provides valuable guidance for the nanocomposite research approach. The experimental results on  $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$  superlattices and  $\text{PbTe}/\text{PbSeTe}$  quantum dots superlattices suggests that by properly choosing the mismatch in electronic properties, the electron transport properties can be maintained at a level comparable to bulk materials or even enhanced using interfaces as energy filters or energy quantization barriers [13]. It is found that the thermal conductivity reduction, rather than the improvement in electrical properties, is the major mechanism behind the enhanced figure of merit in ESS systems. More importantly, the periodic structures are not necessary for thermal conductivity reduction, which prompted more scalable and cost effective nanocomposite approach that shall be addressed in the following.

The nanocomposites covered in this paper have two major categories. The first category is the nanocomposite that is composed of pure nanomaterials. The second category is a system with nanostructures embedded in a host bulk matrix, which is the main stream of nanocomposite approach. Limited by the length of text, this paper can not be a complete coverage of this emerging and fast developing direction.

One of the earliest TE nanocomposites was made by hotpressing the mixture of  $\text{Bi}_2\text{Te}_3$  nanowire/nanotube (Fig.

1) and  $\text{Bi}_2\text{Te}_3$  microsize powder. As  $\text{Bi}_2\text{Te}_3$  works in the temperature range near room temperature, the stability of the nanoinclusion is not a concern. In this work, Zhao et al.[14] reported a 25% increase in ZT (Fig. 2) compared to the homogenous zone-melted bulk sample due to reduced effective thermal conductivity. In a recent work, Gothard et al.[15] studied a hotpressed mixture of nanosized and micro-sized  $\text{Bi}_2\text{Te}_3$  powder. Again, the thermal conductivity is significantly reduced. But the electrical conductivity is deteriorated so much that there is no improvement of ZT. The reason might be that the surface of the  $\text{Bi}_2\text{Te}_3$  nanopowder is passivated during synthesis. The latest advance in  $\text{Bi}_2\text{Te}_3$ -based nanocomposite comes from a surprisingly simple approach: ballmilling the commercial p-type  $\text{Bi}_2\text{Te}_3$  materials in a protective atmosphere and then hotpressing the as-ballmilled nanopowder, the ZT has been increased to  $\sim 1.4$  at 400 K due to not only the reduced thermal conductivity, as expected, but also a slightly improved electrical conductivity [16]. It strongly suggests that the preparation and preservation of the nanoparticles is important to get high ZT.

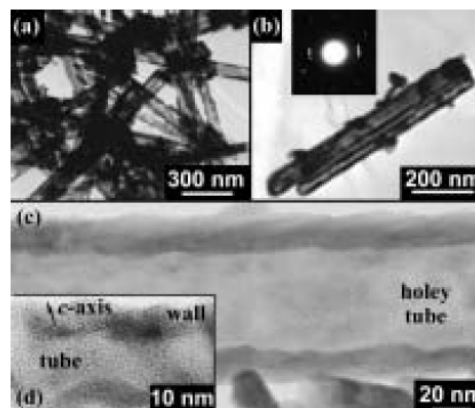


Fig.1 TEM and HRTEM images of the  $\text{Bi}_2\text{Te}_3$  nanotubes hydrothermally synthesized in a hydrothermal environment at  $150^\circ\text{C}$ .

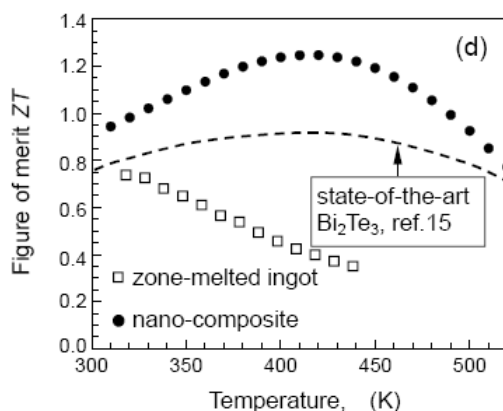


Fig. 2 Temperature dependence of Figure of merit ZT of  $\text{Bi}_2\text{Te}_3$  nanocomposite.

A simple route involving hydrothermal synthesis and hot pressing was used to prepare superlattice-like  $\text{Bi}_2\text{Te}_3\text{-Sb}_2\text{Te}_3$  nanocomposites. [17]. As shown in Fig. 3, the composites have a laminated micro-structure composed of  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  nanolayers with the thickness varying alternately

between 5 and 50 nm. The ZT of such nanocomposite was reported to be 1.47.

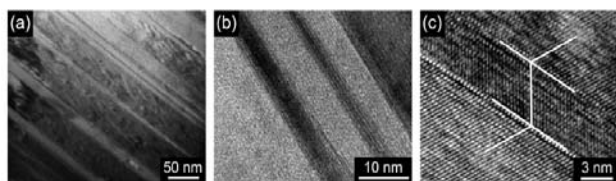


Fig. 3 TEM images of the cross section of the hot-pressed samples show typical laminated nanostructures.

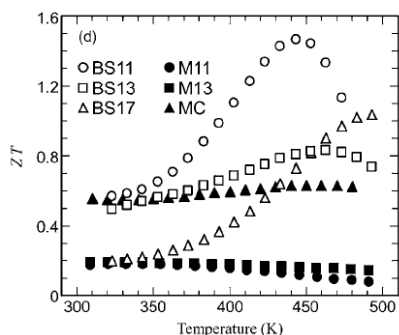


Fig. 4 Temperature dependence of the figure of merit ZT of  $\text{Bi}_2\text{Te}_3$ - $\text{Sb}_2\text{Te}_3$  nanocomposites.

There existed a number of works in  $\text{CoSb}_3$ -based nanocomposites. Mi *et al.* reported a TE study of a hot-pressed mixture of nanosize and microsize  $\text{CoSb}_3$  powders synthesized by hydrothermal method and melting-ballmilling method, respectively. Microstructure analysis shows that the bulk materials are composed of nanosize and microsize grains. A dimensionless figure of merit of 0.71 is obtained for the nanocomposite with 40 wt % nano-inclusions, about 54% increase of that without nano-inclusions, due to significantly reduced thermal conductivity. In another work  $\text{C}_{60}$  has been added as a phonon scatterer at the grain boundary [18]. A significant increase in the thermoelectric figure of merit is achieved for 6.54 mass%  $\text{C}_{60}$  compared to the pure  $\text{CoSb}_3$  (Fig. 6). All the nanocomposites so far addressed in this paper involve mechanically mixing the nanopowder with microsize powder. Achieving a uniform dispersion of nanopowder in the host matrix is not always an easy task. Applying a modified approach, Alboni *et al.* [19] successfully combined the synthesis of the nano-inclusion and the nano-micro powder mixing process into one step: the  $\text{CoSb}_3$  nanoparticles are hydrothermally grown directly on the surface of the micro-sized grain of  $\text{La}_{0.9}\text{Co}_3\text{Sb}_{12}$ . A much uniform dispersion of nano-inclusions has been achieved, as proved in microscopy study. The much reduced thermal conductivity (Fig. 7 left panel), attributed to the phonon scattering by grain boundary and the “rattler effect”, leads to a considerably improved ZT (Fig. 7 right panel).

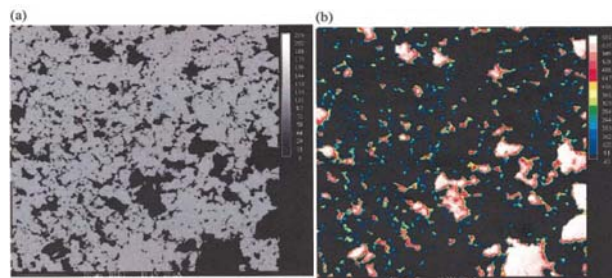


Fig. 5 (a) Backscattered electron image and (b) carbon X-ray map of  $\text{CoSb}_3$  containing 6.54 mass%  $\text{C}_{60}$ .

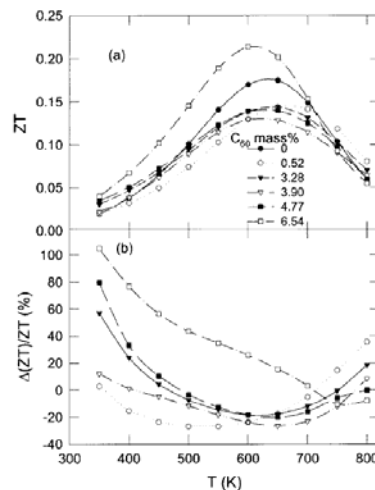


Fig. 6 Temperature dependence of Figure of merit ZT of  $\text{CoSb}_3$  nano-composite.

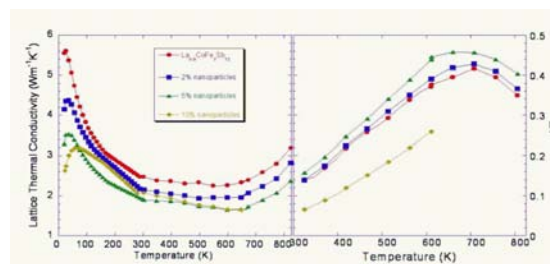


Fig. 7 The temperature dependence of lattice thermal conductivity and the figure of merit ZT of  $\text{CoSb}_3$ -based nanocomposites.

The traditional bulk TE material  $(\text{GeTe})_x(\text{AgSbTe}_2)_{100-x}$  compounds, namely (TAGS-x) materials, have been long known to have good TE performance due to exceptionally low thermal conductivity. However, there is limited effort to study the origin from the micro-morphology point of view. In one recent study, Yang *et al.* [20] found that at 720 K the ZT reaches the state-of-the-art value of 1.53 for TAGS-75, and 1.50 for TAGS-80 and TAGS-85 samples, but the ZT of the TAGS-90 sample is only 0.50 (Fig. 8). Utilizing high-resolution transmission electron microscope and selected area electron diffraction techniques, the authors identified a considerable number of nanoscale domains with typical size  $\sim 10$  nm in the samples that show high ZT values (Fig. 9), and no nanodomain was found in TAGS-90. It is suggested that the presence of nanoscale domains, like the situation in  $\text{PbTe-AgSbTe}_2$  compounds (namely, LAST compounds) [21],

should contribute to the low lattice thermal conductivity of TAGS compounds due to the enhanced mid-frequency phonon scattering. It should be noted that the nanodomains in TAGS materials are *in situ* formed.

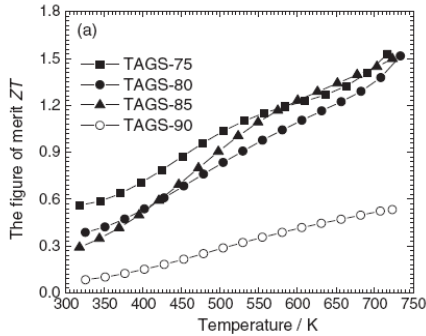


Fig. 8 Temperature dependence of the figure of merit ZT of TAGS-x nanocomposites.

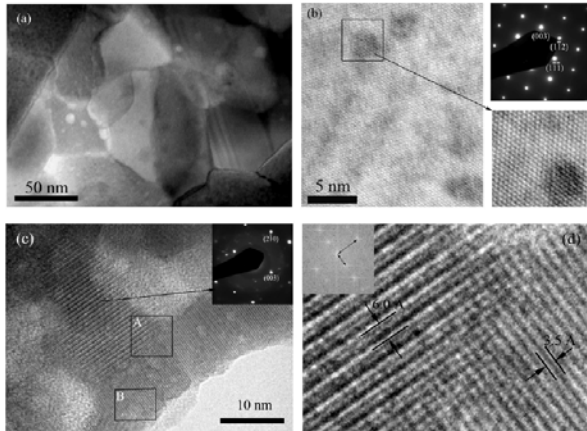


Fig. 9 HRTEM images for TAGS-80. (a) shows nanosized domains in the host matrix. (b) exhibits different areas and SAED patterns. Despite the grey scale variation, there is no difference in lattice symmetry or composition. It is noteworthy that (b) also represents the typical morphology that we observed in TAGS-90. (c) displays nanodomains about 10 nm with different crystal orientation. Regions A and B are the joint areas of different domains. Inserted SAED pattern in (c) indicates there are two sets electron diffraction spots with zone axis  $[1\ 2\ 0]$ . (d) is magnified region A with Fourier transformation pattern as an inset.

Another advance in understanding the thermal transport in nanocomposite materials comes from the SiGe-based material. Yang *et al.* have applied a Monte Carlo simulation technique to estimate the effects of embedded nanostructures in the Ge matrix, and found that the calculation underpredicted the effect of interface for thermal conductivity reduction. It has been attributed to that the Fourier heat conduction theory do not hold for the nanoscale constituent as the phonon mean free path is longer than the characteristic length of nanoinclusion. In his work, the interfacial area per unit volume, instead of the particle size, was pointed out to be the control variable. [18,19] As the interface effects become more and more dominant in the nanocomposites, one need to, theoretically and experimentally, determine the contribution from the interface. We would like to point out that the Hashin-

Shtrikman model provides a good start point of estimating the contribution from the interface [22].

Above we present a number of nanocomposites that have embedded nanostructures in a bulk host matrix or are composed of pure nanostructures. Actually nanocomposite is not conceptually limited in these morphologies. For example, one can introduce two-dimensional nanostructures into a bulk host matrix material using a hydrothermal coating technique. As shown in Fig. 10, Zhang *et al.* hydrothermally coated a nanolayer of PbSnTeSe on the PbSnTe grain [23]. Compared to the conventional preparation of the nanocomposite thermoelectric materials, the salient advantage of this “coating” technique is that one is able to achieve a more homogenous dispersion of the nanostructures, which should subsequently result in more desirable effects on both the thermal and electrical transports via the direct control of the grain boundary. The detailed study is undergoing.

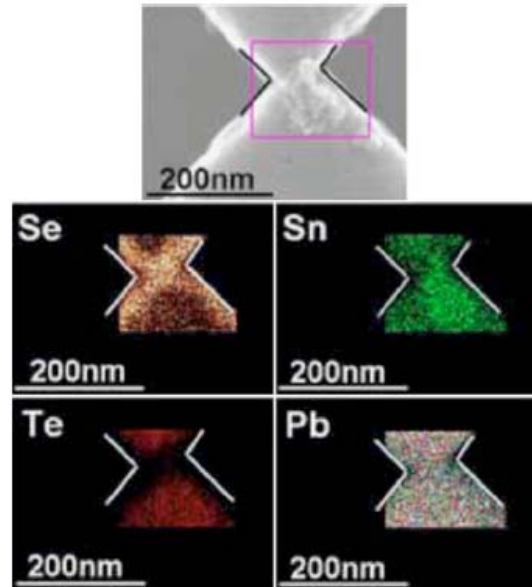


Fig. 10 Spatial elemental distribution is shown, wherein the elemental constituents clearly indicate the formation of a uniform thin layer of  $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Se}$  outside  $\text{Pb}_{0.75}\text{Sn}_{0.25}$  grain.

Also in  $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te}$  system, a different grain boundary engineering approach has been tried. Alkali metal (Na, K) hydrothermal treatments were performed on the microsize  $\text{Pb}_{0.75}\text{Sn}_{0.25}\text{Te}$  bulk grains. After treatment, many Te nanorods with diameters of  $\sim 20$  nm and length of up to 200 nm were found to be uniformly embedded into the surface of bulk grain. As shown in Fig. 11, these nanorod-containing surfaces were subsequently transformed into nano-sized fractal granular grain boundaries upon hot pressing. The presence of this nano-scaled grain boundary results in an improvement of the electrical conductivity to thermal conductivity ratio, via significantly reducing the lattice thermal conductivity without appreciably affecting the Seebeck coefficient and the electrical resistivity. As shown in Fig. 12, the ZT is improved from 0.40 to 0.55 in Na-processed sample at  $\sim 475$  K (425 K). The work provides a novel avenue by which the lattice thermal conductivity of a polycrystalline system, especially

those electrical conductivity relies on mobility so reducing grain size would deteriorate the electrical conductivity (in contrast to the aforementioned half-Heusler compounds), can be “decoupled” from the electronic properties and thus independently “tuned” via controlling the micro-morphology of the inter-grain boundary. [11] In this work, phonon is scattered via three different channels: atomic mass fluctuation due to Sn and Se substitution, grain boundary acoustic mismatch due to the different lattice constant of bulk grain and coated layer, as well as diffusive scattering due to the fractal grain boundary.

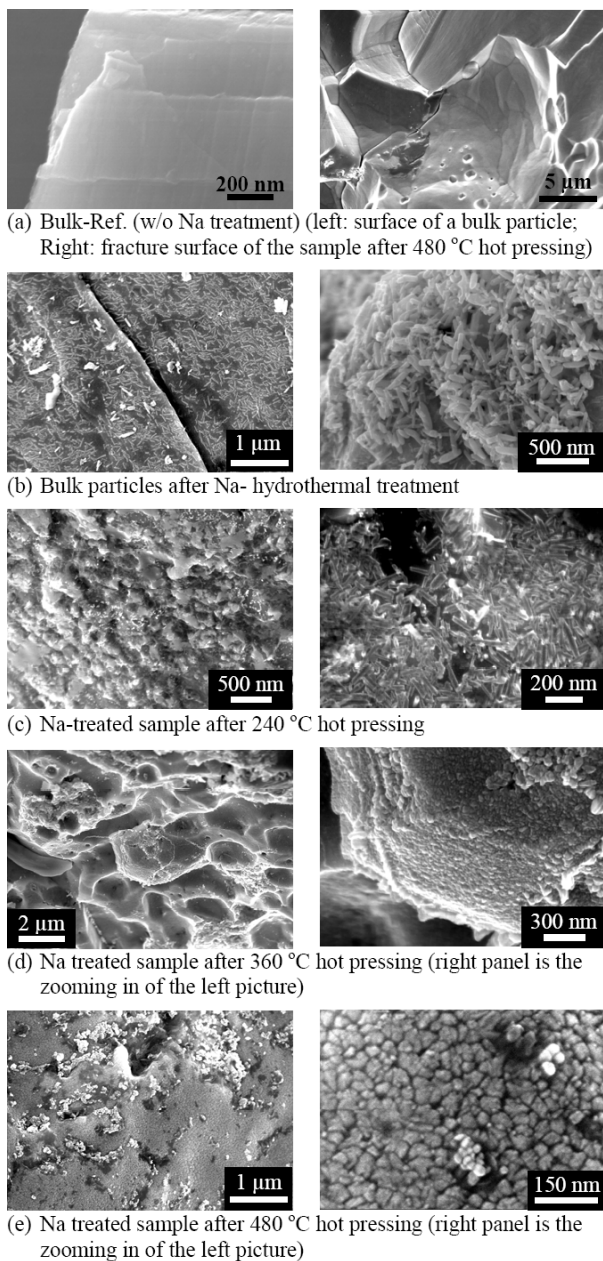


Fig. 11 The SEM images of Na treated  $Pb_{0.75}Sn_{0.25}Te$  bulk particles.

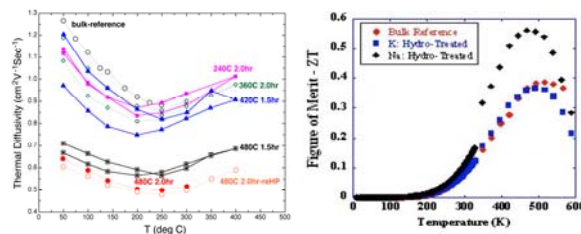


Fig. 12 Temperature dependences of the thermal diffusivity and the figure of merit ZT of Alkali metal treated  $Pb_{0.75}Sn_{0.25}Te$  samples. The thermal diffusivity decreased greatly and ZT increased about 50% compared with the bulk reference sample.

An important issue with nanocomposite material synthesis is to preserve the nanostructure through the synthesis stage. At least, long time high temperature process should be avoided, and, that is part of the reason that a novel processing technique called spark plasma sintering attracts lots of interest. [24] The nanostructures needs to be handled in a protective atmosphere. [16] Also the compacting density of sample is a concern when the nano-content is above 10%. For these reasons, generating the nanostructure *in situ* is the option but the control is more challenging. There are some effort of *in situ* forming nanocomposites, for instance, in  $PbTe/Sb_2Te_3$  system [25],  $Mg_2Si-Mg_2Sn$  system [26] and in the famous LAST system [21].

## Concluding remarks

The significant progress in fabrication, characterization and understanding of the nanoscale thermoelectric (TE) systems, as well as the novel preparative technique of nanocomposite, brought about the feasibility of making nanocomposites. At the present time making and investigating nanocomposites is becoming one of the most active efforts in thermoelectric study. Many research groups all over the world are involved.

There are several ideas behind using nanocomposite concept for enhancing thermoelectric performance. The nanosize constituents introduce numerous interfaces (grain boundary interfaces) that are designed to: 1) scatter phonon more than electron, and 2) to increase the Seebeck coefficient, if possible, via carrier-energy filtering or quantum confinement more than increasing the electrical resistivity. It proved to be a cost effective way to make high performance TE materials.

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