988 *Chem. Mater.* **2010,** *22,* 988–993
DOI:10.1021/cm901862m

CHEMISTRY OF
MATERIALS
Article

Microstructure Engineering Design for Thermoelectric Materials: An Approach to Minimize Thermal Diffusivity[†]

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Received June 29, 2009. Revised Manuscript Received September 2, 2009

An alloy engineering approach aiming to produce a fine two-phase mixture thermoelectric material is highlighted in order to reduce the thermal diffusivity. We utilized the spinodal decomposition in the PbTe-GeTe quasi-binary system to control the alloy microstructure through solutioning, quenching and aging treatments. The effect of various microstructural states on the thermal diffusivity is analyzed. It is observed that a minimum in thermal diffusivity is obtained when several microstructural contributions are combined.

1. Introduction

The phenomenon of thermoelectricity provides a direct mean of converting electricity to a temperature gradient; therefore, this technology is used for cooling or for power generation from heat. Efficiency of thermoelectric devices depends upon a combination of material properties known as the figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, T the temperature, and κ the thermal conductivity. Materials currently commercially available exhibit ZT values around 0.8, which corresponds to less than 20% of the maximum possible Carnot efficiency.[1]

After many years of research, only few materials with ZT above 1 have been produced because the requirements placed on thermoelectric materials are difficult to satisfy; a good thermoelectric material must have high value of Seebeck coefficient while presenting extremely low thermal conductivity and high electrical conductivity. Clearly, few materials can bring together these rather incompatible properties. The best compromise is obtained with narrow band gap semiconductors made of weakly bounded heavy elements, such as bismuth telluride, Bi_2Te_3, with $ZT = 0.9$ and lead telluride, PbTe, with $ZT = 0.8$.[2,3]

Because heat is carried by electrons and lattice vibrations, the challenge to lower thermal conductivity without affecting electrical conductivity leads to strategy that consists to scatter the phonons responsible for the lattice component of thermal conductivity. This strategy has been translated by solid-state chemistry design into materials in which short-wavelength phonons are scattered by atomic scale defects such as interstitial, substitution, vacancies and rattlers. Although this crystal lattice engineering approach has provided good results and new monolithic thermoelectric materials, it affects only a portion of the phonon spectrum.

More recently, it has been shown that the formation of heterostructures at nanoscale provides a scattering mechanism for mid to long wavelength phonons.[4,5] Because the phonon mean free path is larger than for the electrons, the manipulation of the material microstructure offers new degrees of freedom to tune thermal conductivity with weak side effects on electrical properties. This so-called microstructure engineering design has already lead to some successful examples, mainly divided into two types of materials. The first type consists of artificial structures such as Bi_2Te_3/Sb_2Te_3, $Bi_2Te_3/Bi_2(Se,Te)_3$ and PbTe/PbTeSe thin-film superlattices grown by low temperature metal-organic chemical vapor deposition or thermal evaporation−condensation technique (ZT = 2.4 at 300 K) [6,7], and PbSeTe/PbTe quantum-dot superlattice (QDSL) grown by molecular-beam epitaxy (ZT = 1.6 at 300 K and 3 at 550 K) [8−11]. Natural structures represent the second type of materials. In this case, the occurrence of phase transformation during the material synthesis or postprocessing leads to the formation of a second phase.

[†] Accepted as part of the 2010 "Materials Chemistry of Energy Conversion Special Issue".

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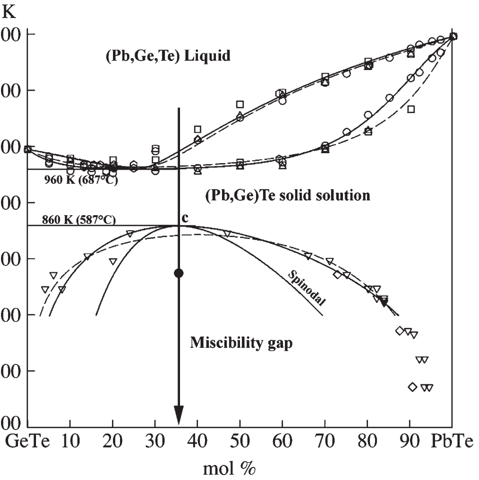

Figure 1. Quasibinary PbTe-GeTe phase diagram according to [15,16]. It consists of the (Pb,Ge,Te) liquid phase, the (Pb,Ge)Te solid-solution phase, and a miscibility gap below 587 °C (860 K). The coordinates of the critical point, *c*, are 36 mol % PbTe and 860 K. The black circle marker represents the position of the alloy during aging inside the spinodal.

Barabash et al. [12] indicate that low thermal conductivity of $AgPb_mSbTe_{m+2}$ alloys [13] arises from the formation of coherent precipitates of $AgSbTe_2$ within PbTe. Utilizing the decomposition of metastable $Pb_2Sb_6Te_{11}$ phase, Ikeda et al. [14] produced a layered two-phase mixture of PbTe and Sb_2Te_3.

There are three main ways to obtain a fine multiphase nanostructured material using solid state phase transformations: (1) the precipitation of a metastable supersaturated solid solution via nucleation and growth processes, (2) the decomposition of an instable solid solution via spinodal decomposition mechanism, and (3) the eutectoid transformation which probably occurred in $Pb_2Sb_6Te_{11}$ alloy studied by Ikeda et al.[14] based on its microstructure and the heat treatments used. In all cases, microstructure features (i.e., size and population density of the second phase) depend upon the diffusion kinetics and the thermodynamic driving forces. They can be manipulated both through the temperature and time of the heat treatment, and the degree of supersaturation of the solid phase via composition tuning.

In this paper, we highlight an alloy engineering design approach to produce multiphase composite materials aiming to reduce thermal conductivity through nanoscaled point defect and boundary scattering effects. The approach is applied to the Pb−Ge−Te ternary system because of the occurrence of a spinodal decomposition that can be used to develop a fine two-phase mixture through the decomposition of the supersaturated solid solution. The experimental investigations intend to produce various microstructural states and to characterize their thermal diffusivity.

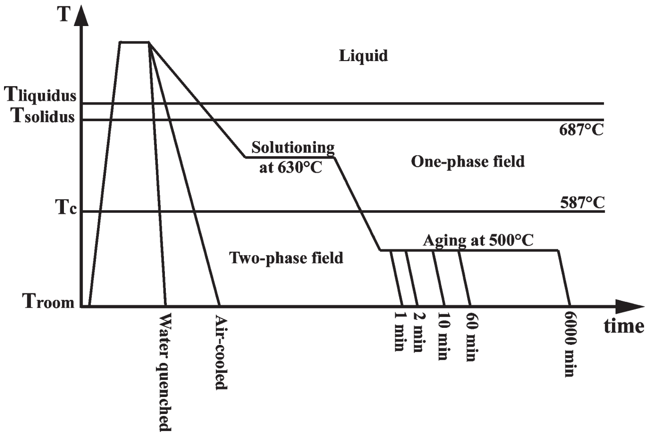

Figure 2. Heat treatments performed on the ternary alloys.

2. Experimental Section

The topology of the PbTe-GeTe quasibinary phase diagram presents an interesting feature for the present purpose (Figure 1).[15,16] It consists of unlimited mutual solubility of its end-members at high temperature in both liquid and solid states. The (Pb,Ge)Te solid solution unmixes below 587 °C (860 K) to one Ge-rich and one Pb-rich tellurides having the NaCl structure (noted GeTe(Pb) and PbTe(Ge) for convenience). Pure PbTe and β-GeTe phases crystallize in a NaCl structure. GeTe presents another allotropic variety below 430 °C, called α-GeTe.

The experiments were performed on an alloy with the critical composition $Pb_{0.36}Ge_{0.64}Te$. This composition was designed so that on cooling, the alloy goes through the top of the miscibility gap (critical point). Samples were prepared by melting Pb (99.99%), Ge (99.999%), and Te (99.99%) in quartz tubes sealed under vacuum. In order to ensure homogeneity, the melt was slowly cooled inside the furnace to 630 °C (above T_c), solution treated at this temperature (inside the one-phase field) during four days and water quenched to freeze the high-temperature solid solution into an unstable supersaturated state. The ingot was cut into several pieces for different isothermal aging treatments at 500 °C performed from 1 to 6000 min in sealed quartz tubes under vacuum. The sequence of solutioning, quenching and aging heat treatments aims to put the alloy inside the unstable region delimited by the spinodal curve into the miscibility gap. The expectation is that the alloy decomposes to a mixture of both solid solution PbTe(Ge) and GeTe(Pb) having stable compositions, one on each side of the miscibility gap.

In addition to these processing conditions, two others samples with identical composition were prepared as-cast−air-cooled and water quenched from the melt−in order to verify the influence of cooling conditions. Figure 2 summarizes the synthesis conditions of the $Pb_{0.36}Ge_{0.64}Te$ samples. Pure PbTe and GeTe phases were also synthesized by casting as reference samples.

Metallographic examination was performed by scanning electron microscopy (SEM) on polished samples at each stage of the thermal treatment. Phase identification was made using X-ray diffraction (XDR) and energy dispersive using X-ray (EDX). The thermal diffusivity (α) was determined at room temperature as a function of the aging time by the flash

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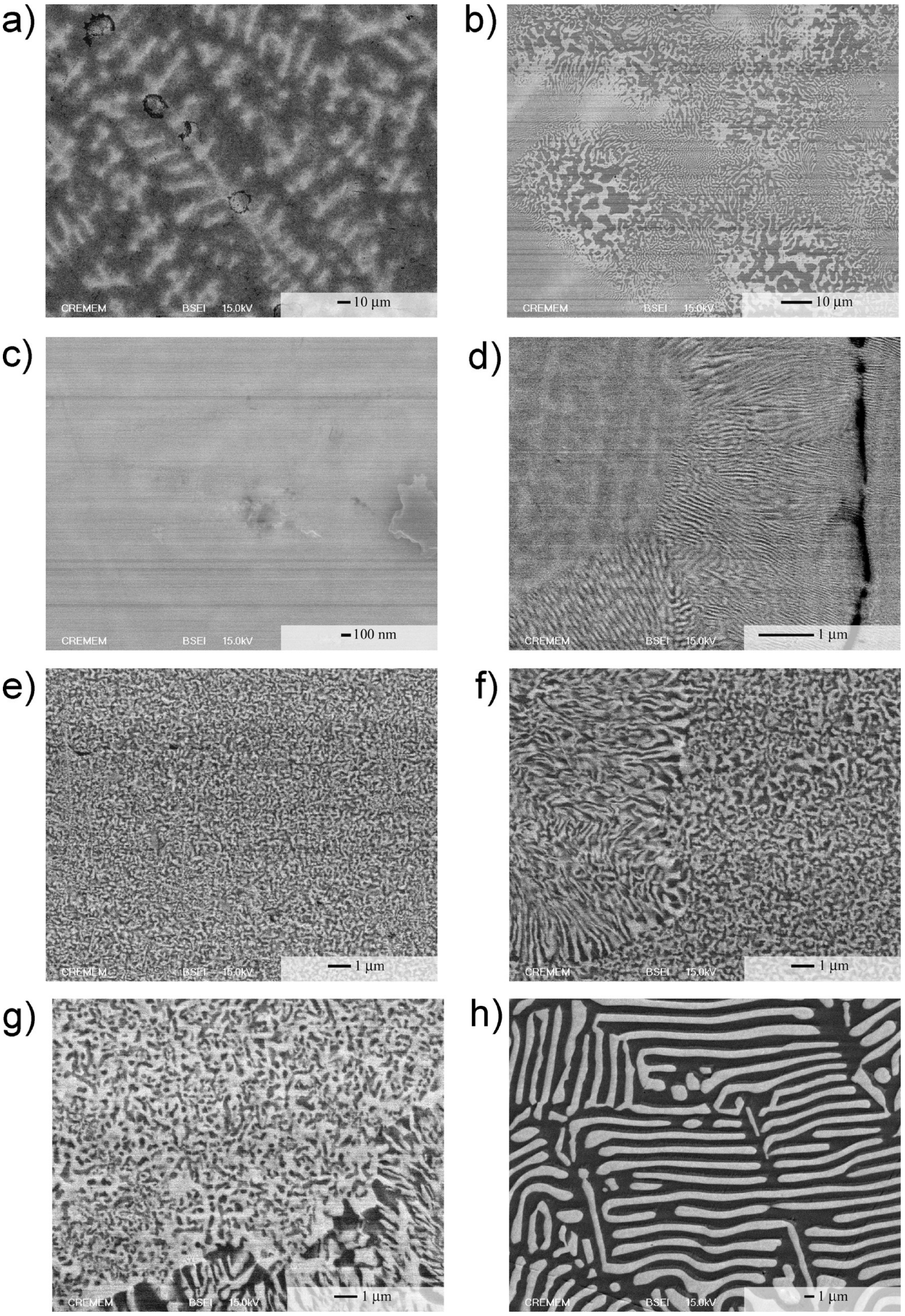

Figure 3. SEM-BSE images of an $Pb_{0.36}Ge_{0.64}Te$ alloy in the (a) quenched from the melt, (b) air-cooled from the melt, (c) solution treated at 630 °C and quenched, (d) solution treated, quenched, and aged at 500 °C for 1 min, (e) for 2 min, (f) for 10 min, (g) for 60 min, and (h) for 6000 min states. The bright and dark phases are PbTe(Ge) and GeTe(Pb), respectively. Image magnifications depend on the microstructure size, they are ranked from the highest to the lowest as: $c > d > e = f = g > h > b > a$.

diffusivity method on disk-shaped samples ($Ø = 6$ mm; thickness ≈ 4 mm). Twenty measurements per samples were performed.

3. Results and Discussion

SEM backscattered electron (BSE) images of the $Pb_{0.36}Ge_{0.64}Te$ alloy in the (a) quenched from the melt, (b) air-cooled from the melt, (c) solution treated at 630 °C and quenched, (d) solution treated, quenched, and aged at 500 °C for 1 min, (e) for 2 min, (f) for 10 min, (g) for 60 min, and (h) for 6000 min states are shown in Figure 3a–h. In BSE images, the phases of highest mean atomic number (Pb content) appear brightest in the images. Phase identification was made using EDX-SEM and XRD techniques. The XRD patterns from the microstructural states presented in Figure 3c–h are shown in Figure 4. All the peaks belong either to the PbTe(Ge), GeTe(Pb) and/or the supersaturated (Pb,Ge)Te solid solutions. In the sample aged at 500 °C for 6000 min (Figure 3h), the composition of the white phase is 10Ge-40Pb-50Te (at %) and the black phase is 39Ge-6Pb-55Te (at %), corresponding to the Pb-rich and Ge-rich regions (noted

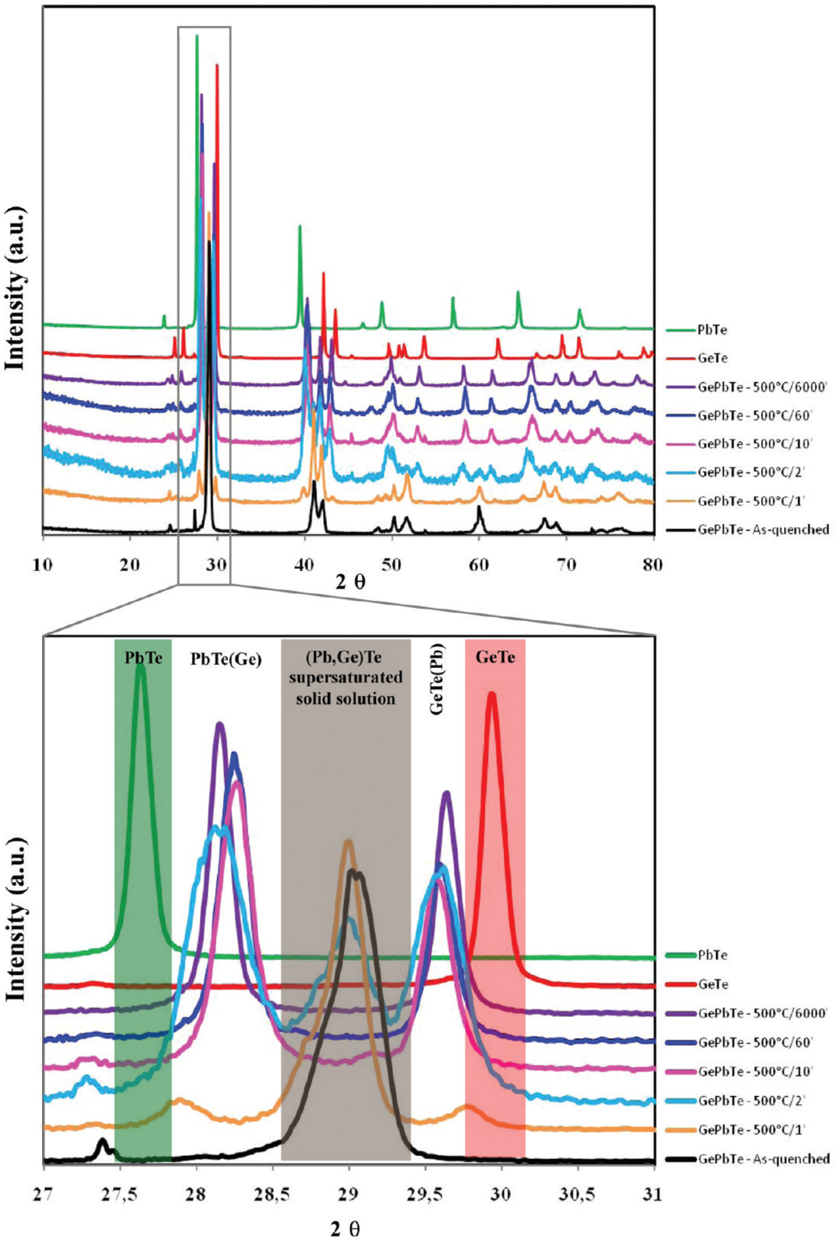

Figure 4. XRD patterns of the $Pb_{0.36}Ge_{0.64}Te$ from the microstructural states shown in Figure 3c−h, along with those of the end-members (pure chalcogenides PbTe and β-GeTe).

PbTe(Ge) and GeTe(Pb)) of the miscibility gap, respectively, in agreement with the phase diagram (Figure 1). The sample quenched from the melt consists of GeTe(Pb) matrix phase formed along with dendrites of PbTe(Ge) (Figure 3a). The one slowly cooled from the melt consists of an inhomogeneous mixture of PbTe(Ge) and GeTe(Pb) with several microstructural features and sizes (Figure 3b). The sample solution treated then quenched consists of the (Pb,Ge)Te supersaturated solid solution phase (Figure 3c) having the nominal composition of the alloy. These results show the strong influence of the cooling condition on the microstructure. Quenching from the melt does not avoid dendrite solidification of PbTe(Ge) when crossing the liquidus, and the air-cooled sample exhibits an inhomogeneous microstructure arising both from the solidification path and the solid state decomposition. Solution treatment inside the one-phase field followed by quenching are both steps of the heat treatment allowing to obtain an alloy made of one-single supersaturated solid-solution phase and ensure microstructure homogeneity during postprocessing treatments.

Short time aged samples (Figure 3d−e) are composed of the supersaturated (Pb,Ge)Te solid solution and a mixture of PbTe(Ge) and GeTe(Pb) precipitates of 50 nm in size. On further aging (Figure 3f-g), Pb-rich and Ge-rich regions grow up to form a coarsened−one micrometer thick− lamellar microstructure (Figure 3h).

These SEM observations are well-confirmed by XRD analysis (Figure 4). After solutioning, only the peaks from the supersaturated solid solution are detected at 2θ angles between those of pure PbTe and β-GeTe phases, as shown for the main peak in the zoom of Figure 4. During aging up to 2 min, the main peak of PbTe(Ge) and GeTe(Pb) appear, respectively, at lower and higher angles than the

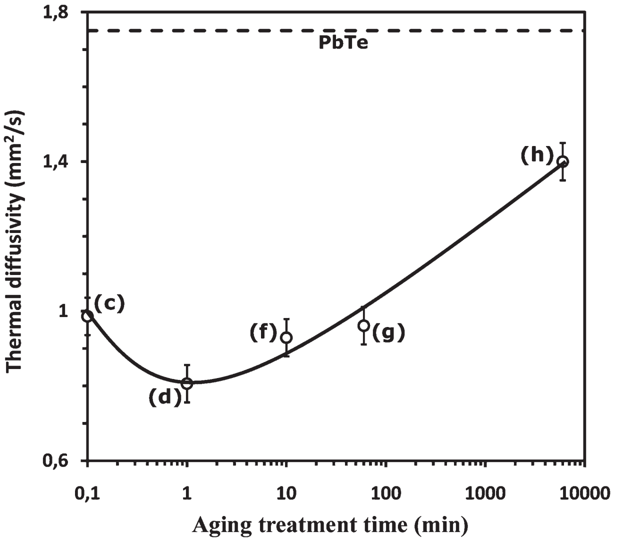

Figure 5. Thermal diffusivity of the $Pb_{0.36}Ge_{0.64}Te$ alloy according the aging time of the heat treatment at 500 °C aimed to decompose the supersaturated solid solution. The dashed line indicates the thermal diffusivity of PbTe. Letters in parentheses are related to the microstructural features shown in Figure 3.

(Pb,Ge)Te main peak. On prolonged aging, peaks of the supersaturated solid solution disappear whereas those of PbTe(Ge) and GeTe(Pb) are enhanced and shifted to lower and higher angles, respectively, as both phases progressively reach their equilibrium compositions as indicated in the phase diagram. At very short aging times (less than 2 min), such a trend is inversed. This can be attributed to the strong stress/strain field possibly generated at the precipitates/matrix interface during the early stage of the spinodal decomposition. This effect is especially strong if precipitates are small and coherent with the matrix, which is usually the case with spinodal decomposition.

From these results, the microstructural changes occurring in the solutioned $Pb_{0.36}Ge_{0.64}Te$ alloy during thermal processing (aging at 500 °C) inside the spinodal region can be explained as the continuous decomposition of the supersaturated (Pb,Ge)Te solid solution to a finely dispersed two-phase mixture of Pb-rich and Ge-rich regions. The designed sequence of heat treatments including solutioning, quenching and aging allow us to obtain the desired multiphase nanostructured materials and to modify its microstructure.

Table 1. Thermal Diffusivities of the Alloys Prepared in This Study, Measured Using the Flash Diffusivity Method and Calculated According To the Rule of Mixtures[a] and Inverse Rule of Mixtures[b] for a Mixture of PbTe and β-GeTe with a Volume Fraction of 40% of PbTe[c]

alloy	state	α (mm²/s)
PbTe	as-cast	1.8
GeTe	as-cast	5.0
rule of mixtures		3.6
inverse rule of mixtures		2.8
$Pb_{0.36}Ge_{0.64}Te$	solution treated and quenched	1.0
	aged 500 °C for 1 min	0.8
	aged 500 °C for 10 min	0.9
	aged 500 °C for 60 min	1.0
	aged 500 °C for 6000 min	1.4
PbTe from the literature		1.7

[a] $\sum p_i f_i$, where p, f, and i stand for the property, the volume fraction, and the constituent, respectively. [b] $\{\sum(f_i/p_i)\}^{-1}$, where p, f, and i stand for the property, the volume fraction, and the constituent, respectively. [c] The value of the thermal diffusivity of PbTe from the literature, presented in the last line of the table, was calculated according the relationship $\alpha = \kappa/C_p\rho$ with $C_p = 155\ \mathrm{J\,kg^{-1}\,K^{-1}}$,[17] $\rho = 8150\ \mathrm{kg\,m^{-3}}$,[17] and $\kappa = 2.14\ \mathrm{W\,m^{-1}\,K^{-1}}$.[18]

Figure 5 and Table 1 show how these microstructural changes affect the thermal diffusivity of the alloy. All samples are found below the thermal diffusivity of the weakest conductor constituent, i.e., PbTe for which the present value is in agreement with the literature (Table 1). The obtained value of 0.8 mm²/s for the thermal diffusivity of the microstructural state in Figure 3d is less than a quarter of the value calculated from the rule of mixtures (3,6 mm²/s) and a third of the inverse rule of mixtures (2,8 mm²/s), both applied between PbTe and GeTe with volume fractions calculated from the tieline at 500 °C. Diffusivity decreases first at short aging time, goes through a minimum for the sample aged 1 min, and increases on further aging. These results show the influence of two contributions to the thermal diffusivity of the alloy: (i) the phonon scattering mechanism due to disorder arising from solute atoms in solution; it is maximum in the solutioned alloy where all the solute atoms are in solution, and it decreases as the solutes leave the supersaturated solid solution to produce enriched regions during the spinodal decomposition; (ii) the phonon scattering due to precipitates and interfaces developed during the decomposition of the supersaturated solid solution; it decreases as the precipitate density and the interface surface drop down, which happens during prolonged aging treatments. The lowest diffusivity is observed at early stage of decomposition (alloy aged during 1 min, Figure 3d) when a nanoscale dispersion of two-phase mixture together with a high supersaturation of the solid solution give rise to the highest point defect density both at the atomic and nanoscale levels. On the basis of the estimation that phonon free path ranges between 1 and 10 nm in this class of materials, and because the microstructural features scale around 50 nm, the slight decreases observed in thermal diffusivity during the early stage of precipitation can be further enhanced if nucleation is favored over growth to give rise to a finer microstructure. This can be achieved through aging treatment performed at lower temperature, where thermodynamic driving forces of precipitation are higher and chemical diffusion is slowed down.

Thermal conductivity, which is the product of thermal diffusivity and two microstructure independent properties, i.e., the heat capacity and the density, should exhibit the same dependence upon the microstructure as the thermal diffusivity. Electrical conductivity is expected to increase at an early stage of aging, whereas the solute atoms leave the supersaturated solid solution, and stay

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unchanged for further aging as soon as the phases have reached their equilibrium composition, because the electron mean free path is typically less than 1 nm for this class of materials.

Overall, it has been shown that the microstructure offers an additional degree of freedom to design thermoelectric materials and manipulate their thermal properties and as a consequence enhance their performance.

4. Conclusion

The sequential steps of solutioning, quenching, and further aging heat treatments of $Pb_{0.36}Ge_{0.64}Te$ alloy effectively decompose the supersaturated solid solution (Pb,Ge)Te into different microstructural states going from dispersed nanosized precipitates to a multiphase composite material with lamellar microstructure composed of GeTe(Pb) and PbTe(Ge) phases. For all the samples, the thermal diffusivity was lower than the weakest conductor constituent (PbTe), with a minimum for the 1 min aged sample; in this case, both the fine nanoscale dispersion and the solute atoms in solution contribute to phonon scattering and as consequence, minimize thermal diffusivity. It is suggested that a further decrease in thermal diffusivity can be achieved by performing aging heat treatments at a lower temperature to favor nucleation over growth.