Structural, Thermal, Optical, and Photoacoustic Study of Mechanically Alloyed Nanocrystalline SnTe

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A nanostructured SnTe phase was produced by mechanical alloying after 2 h of milling. Part of the as-milled powder was annealed and its X-ray diffraction (XRD) pattern was recorded. The XRD patterns of the as-milled and annealed samples were refined using the Rietveld method. After annealing, partial decomposition of the SnTe phase was observed and corroborated by estimating the mean crystallite size using a Willans-Warren plot. The Cowley-Warren parameter \( \text{SnTe}_{\text{CW}} \) for the first coordination shell was calculated, showing a preference for homopolar pairs. This preference is consistent with the partial decomposition observed. According to the optical absorbance spectra, the band gap energy is inversely proportional to crystallite size, following a decaying exponential function. From the photoacoustic absorption spectroscopy measurements, the thermal diffusivity parameter and the transport properties of as-milled and annealed SnTe powder were determined.

Keywords: Semiconductors, Nanocrystals, Mechanical alloying, Thermoelectric materials, X-ray diffraction, Photoacoustic absorption spectroscopy.

1. Introduction

Chalcogenide semiconductor compounds are of considerable interest due to their optical\(^1\), electronic\(^2\), and optoelectronic\(^3\) applications. In particular, the tin telluride (SnTe) compound has potential applications in mid-infrared (3-14 \( \mu \)m) detection and thermoelectric conversion\(^4\)-\(^7\).

According to the Inorganic Crystal Structure Database (ICSD)\(^8\), code 188457, at room temperature and atmospheric pressure, the SnTe compound crystallizes in a cubic structure (S.G. Fm\(\overline{3}\)m, \(Z = 4\)), with the Sn atoms occupying the Wyckoff site 4\(a\) (0, 0, 0) and the Te atoms occupying the site 4\(b\) (0.5, 0.5, 0.5). This compound can be synthesized using the techniques of molecular beam epitaxy\(^9\), electrodeposition\(^10\), solution-phase synthesis\(^11\) and mechanical alloying (MA)\(^12\)-\(^13\). MA has been used for synthesizing crystalline compounds, amorphous materials and solid solutions\(^14\)-\(^17\). It has also been used to produce nanostructured materials as well as alloys whose components have large differences in their melting points, making difficult their production through techniques based on fusion\(^18\).

Nanostructured materials are metastable and can be described by two structural components, one containing crystallites with nanometer dimensions (2-100 nm), that have the same structure as the bulk crystalline counterpart, and an interfacial component formed by different kinds of defects (grain boundaries, interphase boundaries, dislocations, etc.)\(^19\). Commonly, the volume fractions of the two components are of the same order, leading a strong dependence of the material properties on the atomic arrangements of the interfacial phase\(^19\). Manipulation of these atomic arrangements leads to the possibility of designing new materials with the properties required for specific technological applications\(^20\).

Since MA yields materials containing a high concentration of defect centers, it is interesting to investigate the influence of concentration of defect centers on the structural, optical, thermal, and photoacoustic properties of SnTe. For this, the X-ray diffraction (XRD), differential scanning calorimetry (DSC), optical absorbance (UV-VIS-NIR), and photoacoustic absorption spectroscopy (PAS) techniques were used. This paper reports the results obtained for as-milled and annealed nanostructured SnTe.
2. Determination of mean crystallite size and strain using the Williamson-Hall plot and a pseudo-Voigt function to describe the diffraction line profiles

The diffraction line broadening is well described by a Voigt function, which is described by a convolution of Gaussian and Lorentzian (also called as Cauchy) functions. In a single line analysis, the apparent crystallite size is calculated using the Scherrer formula$^{23} D = \frac{\beta \cos \theta}{\pi} \sin \theta$ and the strain is calculated using the formula$^{25} \sigma = \frac{\beta \cos \theta}{\pi} \sin \theta$ where $\theta$ is the diffraction angle, $\lambda$ is the X-ray wavelength and $\beta_l$ and $\beta_g$ are the Lorentzian and Gaussian integral breadths of the diffraction line. The $\beta_l$ and $\beta_g$ integral breadths are related to full widths at half maximum (FWHM) of the normalized Lorentzian $\Gamma_L$ and Gaussian $\Gamma_G$ components by the expressions $\beta_l = \frac{\Gamma_L}{\pi \ln 2}$ and $\beta_g = \frac{\Gamma_G}{\pi \ln 2}$. The shape of the Voigt function is determined by the relative intensities of the two components. The pseudo-Voigt function, $pV(\chi)$, is an approximation of the Voigt function that substitutes the shape parameters $\Gamma_L$ and $\Gamma_G$ by two other parameters, $\Gamma$ and $\eta$. The function is a linear combination of Lorentzian and Gaussian functions with the same FWHM, $\Gamma$, and a parameter $0.32823 \leq \eta \leq 1$ used to specify the relative intensity of the Lorentzian component.

The relations between the $\Gamma_L$ and Gaussian $\Gamma_G$ of the Voigt function and the $\Gamma$ and $\eta$ of $pV(\chi)$ are given by the expressions,$^{26}$

$$\Gamma_L = (1 - 0.74417\eta - 0.24781\eta^2 - 0.00810\eta^3)^{1/2} \Gamma = c_1 \Gamma \quad (1)$$

and

$$\Gamma_G = (0.72928\eta + 0.19289\eta^2 + 0.07783\eta^3) \Gamma = c_2 \Gamma \quad (2)$$

Using the relations $\beta_l = \frac{\Gamma_L}{\pi \ln 2}$ and $\beta_g = \frac{\Gamma_G}{\pi \ln 2}$, we have $\beta_l + \beta_g = (c_1 \Gamma + c_2 \Gamma) \Gamma$.

$$\frac{0.91 \lambda}{D \cos \theta} + 4 \sigma \tan \theta = (c_1 \Gamma + c_2 \Gamma) \Gamma \quad (3)$$

or

$$\Gamma \cos \theta = \frac{0.91 \lambda}{D(3c_2 \Gamma + c_1 \Gamma)} + \frac{4 \sigma}{c_1 \Gamma + c_2 \Gamma} \sin \theta \quad (4)$$

Expression (4) is the standard equation for a straight line ($y = a + bx$). By plotting $\Gamma \cos \theta$ versus $\sin \theta$ we obtain the mean microstrain component from the slope and the mean crystallite size from the interception with the $\Gamma \cos \theta$ axis. Such plot is known as the Williamson-Hall plot. The $\Gamma$ and $\eta$ values are obtained directly from the Rietveld refinement of the XRD pattern.

A relationship between the crystallite size $D$ and the microstrain $\sigma$ can be obtained due to the fact that $pV(\chi)$ is a linear combination of Lorentzian and Gaussian functions with the same FWHM ($\Gamma$), and

$$D \sigma = \frac{0.91 \lambda c_1 c_2}{4 c_2 c_1 \sin \theta} \quad (5)$$

Eq. (5) should be used in a single line analysis only, i.e., after determining the apparent crystallite size.

3. Experimental Procedure

High-purity elemental powders of tin (Alfa Aesar 99.8 %) and tellurium (Alfa Aesar 99.999 %) were blended with SnTe nominal composition was sealed together with several steel balls of 1.5 cm in diameter into a cylindrical steel vial under argon atmosphere. The ball-to-powder weight ratio was 5:1. MA was performed using an 8000 Spex Mixer/Mill at room temperature, and a ventilation system was used to keep the vial temperature close to room temperature. The milling process was stopped after 2 h when the XRD pattern of the as-milled powder showed an excellent agreement with the pattern given in the ICSD code 188457 for the SnTe phase$^8$. The XRD patterns were recorded using a Philips X-Pert powder diffractometer, using the Cu Kα radiation ($\lambda = 1.5406 \AA$). The XRD patterns were refined using the Rietveld method$^{24}$, implemented in the GSAS package$^{25}$. The XRD pattern of a certified elemental silicon sample was recorded in the same experimental conditions and used to take into account the instrumental broadening for the Rietveld refinements. A $pV(\chi)$ function was used to describe the diffraction lines profiles. Thermal parameter (Uiso) was assumed to be isotropic.

The thermal stability of the SnTe phase was investigated using DSC measurements from room temperature up to 500 °C, with a heating rate of 10 °C/min, under nitrogen flow, using Al pans in a TA Instruments 2010 DSC cell. Based on the thermograms, annealing was carried out on a portion of the as-milled SnTe powder in order to study the influence of concentration of the defect centers on the properties previously mentioned. For this, a pellet of SnTe was inserted into an evacuated quartz tube, which was maintained under low pressure ($\approx 10^{-1}$ Torr) in argon gas. The sample was annealed at 320 °C for 2.5 h, followed by air cooling.

The optical properties of the as-milled and annealed nanostructured SnTe samples were studied using UV-VIS-NIR measurements. The optical transmittance measurements were taken in an energy range of 0.06-0.50 eV, using a Perkin-Elmer FT-IR Spectrometer, Spectrum 100. For measurements, as-milled and annealed powders were dispersed into KBr powder and pressed using the same pressure to form pellets.

The PAS measurements were carried out in an open photoacoustic cell (OPC) setup built at home. Details about the OPC setup can be found in Refs. 26 and 27. The samples for the OPC measurements were prepared by compressing at the same pressure (6 tons) the as-milled and annealed SnTe powders to form tiny circular pellets, 10 mm in diameter, with thickness of 440 µm and 450 µm, respectively. The samples were mounted
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directly onto the front sound inlet of an electret microphone, and periodically illuminated to generate the photoacoustic effects, as described by the thermal diffusion model.

4. Results and Discussion

4.1 XRD and DSC measurements

Figure 1 shows the XRD pattern (black open circles) recorded for 2 h of milling. It was compared with those given in the ICSD Database for the Sn-Te system, and an excellent agreement was observed with that for cubic SnTe (ICSD code No. 188457). Besides the diffraction peaks of SnTe, two low intensity diffraction peaks at about 2θ = 27º and 34º were observed, and indexed to SnO$_2$ (ICSD code 9163). The SnO$_2$ peaks did not appear in the XRD patterns of the Sn and Te powders used to prepare the samples. Then, its nucleation probably occurred during manipulation of the powder to perform the XRD measurements and is probably restricted to the region close to the particle surface. The enthalpies for formation of the SnO$_2$, TeO$_2$, and SnTe phases are -596.429 kJ/mol, -345.503 kJ/mol, and -91.737 kJ/mol, respectively.

The Rietveld refinement does not take into account the contribution of the background to calculate the relative volume fractions of phases composing the experimental XRD pattern. The relative volume fractions were 96 % for SnTe and 4 % for SnO$_2$. The goodness-of-fit indicators $R_p$ and $R_{wp}$ are shown in this figure.

The XRD pattern of as-milled samples shows broad peaks, suggesting that the mean crystallite size $D$ of the SnTe phase is of nanometer dimension. The values of $D$ and of the microstrain $\sigma_p$ were estimated through the Williamson-Hall plot, using a pseudo-Voigt function to describe the profiles of peaks in the Rietveld refinement, as shown in Section 2. The values of $\Gamma$ and $\theta$ were obtained from the Rietveld refinement. Figure 2 shows the $\Gamma \cos \theta$ vs $\sin \theta$ data for the SnTe phase. By fitting the data to a straight line, values of $D = 75.2$ nm and of $\sigma_p = 0.45$ % were obtained.

Figure 2. (color online): Williamson-Hall plot for the as-milled and annealed (inset) SnTe samples

As described in the Section 3, part of the as-milled SnTe powder was annealed in order to study the influence of concentration of the defect centers on the properties previously mentioned. Figure 3 shows the XRD pattern of the annealed sample. The pattern shows, besides the peaks of SnTe and SnO$_2$, low intensity peaks at about 2θ = 27.6º and 38.3º that were indexed to elemental Te (ICSD code 65692). The best Rietveld refinement of this XRD pattern was reached considering the values of lattice parameter $a = 6.3155$ Å, $\eta = 0.328$ for SnTe; $a = b = 4.7390$ Å, $c = 3.1907$ Å, $\eta = 0.328$ for SnO$_2$; and $a = b = 4.4718$ Å (4.456 Å), $c = 5.9167$ Å (5.921 Å), $\eta = 0.328$ for elemental Te. The values within parentheses are those given in the ICSD code 65692. The simulated XRD patterns for the annealed sample and individual patterns for SnTe, SnO$_2$, elemental Te, and the difference between experimental and simulated patterns (bottom line) are shown in Fig. 3, from where one can see an excellent agreement. The relative volume fractions were 77 % for SnTe, 13 % for SnO$_2$, and 10 % for elemental Te. It is
interesting to note that after annealing, the volume fraction of SnTe decreased 19 % and the volume fraction of SnO$_2$ increased 9 %. The goodness-of-fit indicators $R_p$ and $R_{wp}$ are shown in this figure.

Figure 3. (color online): Experimental and simulated XRD patterns of an annealed SnTe sample. The simulated SnTe, SnO$_2$ and elemental Te phases as well as the difference between experimental and simulated patterns (bottom line) are also shown.

As for as-milled SnTe, the values of $D$ and $\sigma_p$ for annealed SnTe were estimated using the Williamson-Hall plot, which is shown in the inset of Fig. 2. By fitting to a straight line, values of $D = 59.3$ nm and $\sigma_p = 0.075$ % were obtained. It is interesting to note that, after annealing, a variation of $\approx 21$ % in the mean crystallite size is observed, and this value is close to the variation in the volume fraction of SnTe (19 %).

Chemical disorder is among the physical mechanisms responsible for phase transformation, amorphization and decomposition of alloys with increasing pressure and/or temperature, but it has not received the attention it deserves. Trying to explain the partial decomposition of nanostructured SnTe under annealing, the influence of chemical disorder was investigated. The Cowley-Warren chemical short-range order (CSRO) parameter $\alpha_{CW}$, used to study the statistical distribution of atoms in solids, is given by $29$

$$\alpha_{CW} = 1 - \frac{N_{ij}}{c_i c_f (N_{ii} + N_{jj}) + c_i c_j (N_{ij} + N_{ji})} \quad (6)$$

where $N_{ii}$, $N_{ij}$ and $N_{jj}$ are the coordination numbers and $c_i$ and $c_f$ are the concentrations of atoms of the elements $i$ and $j$. The $\alpha_{CW}$ parameter is zero for a random distribution, negative if there is a preference for forming unlike pairs and positive if homopolar pairs (clusters or local order) are preferred. Although the $\alpha_{CW}$ parameter is usually applied to amorphous phases, it can also be used to determine the relative preference for forming different atomic pairs and thus to investigate the crystallization behavior of a binary alloy. The coordination numbers $N_{SnTe}$, $N_{SnO_2}$, $N_{TeTe}$ and $N_{TeTe}$ were obtained using the structural data given in ICSD 188457 for SnTe in the Crystal Office 98 software$^{29}$ to build the 3D structure, and using the tool "shell structure" the $R_{SnTe}$, $R_{SnO_2}$ and $R_{TeTe}$ interatomic distances were calculated up to 10 Å. By putting the origin at Sn atoms (site 4a), the coordination numbers for the first neighbors are $N_{SnSn} = 12$ at 4.4670 Å and $N_{SnTe} = 6$ at 3.1590 Å. By putting the origin at Te atoms (site 4b), the coordination numbers for the first neighbors are $N_{TeSn} = 6$ at 3.1590 Å and $N_{TeTe} = 12$ at 4.4675 Å. Using the values in Eq. (6), a value of $\alpha_{CW} = 0.333$ is obtained, indicating a preference for forming homopolar pairs in the first coordination shell. This value suggests that the repulsive part of the crystalline field plays an important role in the structural stability of this phase. During annealing, the thermal movements of the Sn and Te atoms may be responsible for introducing structural instability, promoting the partial decomposition of SnTe.

In order to understand the partial decomposition of the SnTe phase under annealing, part of as-milled powder was studied using DSC measurements. Figure 4 shows two sequentially recorded DSC thermograms for the same as-milled sample, and one run for the annealed sample, with a heating rate of 10 °C min$^{-1}$ under nitrogen flow. In the first run (blue top line), one can see an exothermic peak at about 278 °C and a low intensity exothermic broad band between 384 °C and 417 °C. In the second run (black middle line) one can see the previous exothermic peak slightly shifted toward lower temperatures ($\approx 265$ °C), and an endothermic peak at about 392 °C. In the thermogram for the annealed sample (red bottom line), one can see the previous exothermic peak shifted toward higher temperatures ($\approx 291$ °C) and the endothermic peak at about 395 °C, now well-defined and seeming to be formed by two endothermic peaks (see inset).

Figure 4. (color online): DSC thermograms of the as-milled and annealed samples.

In order to analyze the DSC thermograms shown in Fig. 4, the following values of the melting points ($T_m$) are useful: 232.08 °C for Sn, 449.6 °C for Te, 806 °C for SnTe, 1080 °C for SnO, 1727 °C for SnO$_2$, and 188457 for SnTe in the Crystal Office 98 software$^{29}$ to build the 3D structure, and using the tool "shell structure" the $R_{SnTe}$, $R_{SnO_2}$ and $R_{TeTe}$ interatomic distances were calculated up to 10 Å. By putting the origin at Sn atoms (site 4a), the coordination numbers for the first neighbors are $N_{SnSn} = 12$ at 4.4670 Å and $N_{SnTe} = 6$ at 3.1590 Å. By putting the origin at Te atoms (site 4b), the coordination numbers for the first neighbors are $N_{TeSn} = 6$ at 3.1590 Å and $N_{TeTe} = 12$ at 4.4675 Å. Using the values in Eq. (6), a value of $\alpha_{CW} = 0.333$ is obtained, indicating a preference for forming homopolar pairs in the first coordination shell. This value suggests that the repulsive part of the crystalline field plays an important role in the structural stability of this phase. During annealing, the thermal movements of the Sn and Te atoms may be responsible for introducing structural instability, promoting the partial decomposition of SnTe.

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733 °C for TeO₂, and 430 °C for TeO₂. Based on these values, one can see that the endothermic peak at about 395 °C cannot be associated with the fusion of any of the phases above. Youngku Sohn investigated the formation of SnO₂ starting from the decomposition of a Sn-polymer complex. The TG/DSC thermogram shown in Fig. 4 (right) of Ref. 31 displays an endothermic peak at about 395 °C, similar in shape and temperature to the endothermic peak observed in this study, that was attributed to formation of SnO₂. Only in the DSC thermograms of the as-milled (second run) and annealed samples this endothermic peak is observed. On the other hand, the XRD pattern of the annealed sample showed a decrease in the relative volume fraction of SnTe. Thus, we attribute the endothermic peak located between 390 °C and 400 °C to the formation of SnO₂ from Sn atoms originated from the partial decomposition of SnTe under annealing. With respect to the exothermic peak observed between 260 °C and 295 °C in the three thermograms, it can be associated with crystallization from an amorphous phase and/or with a phase transformation. No amorphous phase was observed in the XRD patterns of as-milled and annealed samples; if it exists, its intensity is too low to be separated from the background or from the contribution of the interfacial component (diffuse scattering) to the XRD pattern. Manzato et al. synthesized SnO and SnO₂ by high-energy milling. In the thermogram shown in Fig. 5 of Ref. 32, two exothermic peaks located at about 195 °C and 287 °C were attributed to the formation of SnO and SnO₂, respectively. Thus, we attribute the exothermic peak located between 260 °C and 295 °C to formation of the SnO phase starting from the relaxation of Sn atoms located in the interfacial component of SnTe. Formation of pure Te can be due to the diffusion of Te atoms located at the interfacial component and/or from the partial decomposition of SnTe.

4.2 Optical absorbance measurements

Commonly, the value of the optical band gap energy of a thin film is obtained by McLean analysis of the absorption edge. Another way to obtain the optical band gap energy is presented in Ref. 34. The expression given in Ref. 33 was modified to be applied to a powder; the details are presented in Refs. 35,36 and will not be repeated here. The modified McLean equation is written in the form:

\[ \text{Abs} = A (h\nu - E_g + E_p)^{1/n} \]

where \( A \) is the absorbance, \( h \) is the Planck constant, \( \nu \) is the frequency of the incident beam, \( l \) is an adjustable parameter and \( n \) is an index representing the transition order. A value of \( n = 2 \) corresponds to a direct allowed transition, \( n = 2/3 \) to a direct forbidden transition, \( n = 1/2 \) to an indirect allowed transition and \( n = 1/3 \) to an indirect forbidden transition.

In this study, the transmittance data were converted to absorbance data using the expression \( A = 2 \cdot \log_{10} T \). Figure 5 shows the \((h\nu \times A^2)\) vs photon energy plot for the annealed SnTe sample and the inset (top) shows the absorbance vs photon energy plots for as-milled (red curve) and annealed (blue curve) samples. In the inset one can see that the optical absorption edge of the as-milled sample (red curve) is very broad due to the mean crystallite size of \( D = 75.2 \text{ nm} \) and the microstrain of \( \sigma_p = 0.45% \), as well as the substantial interfacial component. These features hinder the precise determination of the optical band gap energy. On the other hand, the absorbance spectrum for the annealed SnTe sample (blue curve) shows a narrow optical absorption edge, despite decomposition of SnTe promoted by annealing, led to a reduction of the mean crystallite size (\( D = 59.3 \text{ nm} \)). According to the Refs. 37 and 38, SnTe has a direct optical band gap (\( n = 2 \)). Fitting of experimental data to the McLean equation (red straight line) yields a band gap energy of \( E_g = 0.187 \text{ eV} \).

It is interesting to compare the band gap energy for the annealed SnTe sample obtained in this study with other values reported in the literature. Ref. 38 reported a value of \( E_g = 0.54 \text{ eV} \) for nanocrystals SnTe with dimension of 6.5 nm; Ref. 37 reported values of \( E_g = 0.54 \text{ eV} \) and 0.39 eV for nanocrystals SnTe with dimensions of 7.2 nm and 14 nm, respectively; Refs. 38 and 39 reported a value of \( E_g = 0.18 \text{ eV} \) for bulk SnTe (\( D \geq 100 \text{ nm} \)) at room temperature. Figure 6 shows \( E_g \) vs \( D \) data above fitted to an exponential function \( E_g = E_g^0 + A \cdot e^{-D/B} \). This figure suggests that the band gap energy is inversely proportional to the crystallite size and follows an exponential law. Assuming that this behavior is true, the mean crystallite size (\( D = 75.2 \text{ nm} \)) of as-milled sample leads to a value of \( E_g = 0.182 \text{ eV} \). By fixing this value, a fitting of experimental data to the McLean equation (red straight line)
is shown in the inset (bottom) of Fig. 5. A brief theoretical explanation for the behavior observed above is the following: for any isolated X atom, for instance, semimetals (X = Si, Ge) or nonmetals (X = Se), the band gap is equal to the distance between the ground state and the first excited state. Due to the Pauli exclusion principle, both levels are broadened in a solid. This broadening leads to narrowing of the bandgap and, therefore, it is expected that the band gap in a solid be less than in an isolated atom. In nanomaterials, the small number of atoms leads to a smaller interaction between atoms than in a bulk material. Thus, the energy levels are similar to those of isolated atoms. As the number of atoms decreases (i.e., as the volume of the nanomaterial decreases) the energy levels become more similar to those of isolated atoms. A brief quantitative analysis is given by Z.G. Fthenakis.

4.3 PAS measurements

The determination of the thermal diffusivity parameter and/or the transport properties of semiconducting materials using PAS is widely documented in the literature. A theoretical summary of the PAS principles and applications are given in Refs. 41-47 and references therein and will not be repeated here.

The thermal diffusivity for bulk SnTe can be calculated using the expression for the thermal conductivity $k = \rho C_p \alpha$, where $\rho$ is the density, $C_p$ is the specific heat and $\alpha$ is the thermal diffusivity. The TAPP software (version 2.2) gives values of $\rho = 6509 \text{ kg m}^{-3}$ and $C_p = 211 \text{ J kg}^{-1} \text{ K}^{-1}$ for SnTe. Gelbestein reported a value of $K = 7.9 \text{ Wm}^{-1} \text{ K}^{-1}$ for bulk SnTe. Using these values in the expression above, a value of $\alpha_{\text{cal}} = 0.0575 \times 10^{-4} \text{ m}^{-2} \text{s}^{-1}$ (0.0575 cm$^2$ s$^{-1}$) is obtained. Zhang et al. produced an undoped SnTe phase and reported a value of $\alpha_{\text{SnTe}} = 0.056 \text{ cm}^2 \text{s}^{-1}$ for the thermal diffusivity at room temperature. The characteristic frequency $f = \alpha / \pi l^2$, where $l$ is the sample thickness, is the modulation frequency corresponding to the transition from the thermally thin regime ($f < f_0$) to the thermally thick regime ($f > f_0$), where $f$ is the modulation frequency. The thicknesses of the as-milled and annealed samples were 440 and 450 $\mu$m, yielding characteristic frequencies of 11.1 Hz and 10.6 Hz, respectively.

Figure 7 shows the PAS signal amplitudes for as-milled and annealed SnTe and Fig. 8 shows the corresponding signal phases. According to Fig. 7, both signal amplitudes decrease with increasing modulation frequency. A similar behavior is observed in Fig. 8 for the signal phases. We used the procedure described in Ref. 44 to find the contribution of each heat transfer mechanism to the pressure variation in the photoacoustic cell and thus to take into account the contribution of intraband nonradiative thermalization (thermal diffusion). Figure 7 also shows that between 40 and 110 Hz and between 50 and 70 Hz, the PAS signal amplitudes for as-milled and annealed samples are proportional to $f^{-0.9807}$ and $f^{-0.9959}$, respectively, a behavior that may be attributed to nonradiative surface recombination, thermoelastic bending or thermal dilation. Thermal dilation heat transfer mechanisms produce a signal whose phase is independent of the modulation frequency and equal to 90°. Since, according to Fig. 8, the signal phase decreases as the modulation frequency increases, this mechanism can be disregarded. The contribution of nonradiative bulk recombination is proportional to $f^{-1.5}$. Usually, the phase of the photoacoustic signal corresponding to nonradiative bulk recombination exhibits a minimum that corresponds roughly to the point at which the phase dependence changes from $f^{-1.3}$ to $f^{-1.0}$, that is, it marks the transition from bulk to the surface recombination as the dominant mechanism responsible for the photoacoustic signal. This fact is discussed in Ref. 43. On the other hand, as reported by Dramicanin et al. as the sample thickness decreases the minima in both amplitude and phase are shifted to higher frequencies and their intensities around this minimum decrease. It is interesting to note that the positions of these minima depend on the material investigated.

By considering the results reported in Ref. 51 and the sample thicknesses used in this work, it is expected that these minima cannot be observed in the amplitude and phase PAS signals.
Figure 8. (color online): PAS signal phase vs modulation frequency for the as-milled (circles) and annealed (stars) samples. The solid lines are the best fits of the data for as-milled samples to Eq. (8) and of the data for annealed samples to Eq. (9).

In as-milled SnTe, the absence of the contribution of nonradiative bulk and surface recombination heat transfer mechanisms were verified by not being possible to fit the phase data to the phase expression given by Pinto Neto et al.\textsuperscript{43} for these mechanisms, taking the thermal diffusivity value of \( \alpha_{\text{calc}} = 0.0575 \text{ cm}^2\text{s}^{-1} \) as the initial value. On the other hand, the expression for the phase corresponding to the thermoelastic bending heat transfer mechanism\textsuperscript{43-45} written as

\[
\Phi_{\text{ph}} = \phi_0 + \tan^{-1} \left[ \frac{1}{\tilde{\alpha} f - 1} \right]
\]

where \( \tilde{\alpha} = l / \sqrt{\nu} \), \( f \) is the modulation frequency, \( l \) is the sample thickness, and \( \tilde{\alpha} \) its thermal diffusivity, was successfully fitted to the \( \Phi_{\text{ph}} \) versus \( f \) plot in the modulation frequency range of 44-100 Hz. From the best fit, a value of \( \alpha_{\text{eff}} = 0.0825 \text{ cm}^2\text{s}^{-1} \) was obtained for the thermal diffusivity. Similarly, in the annealed sample, the absence of the contribution of nonradiative bulk recombination and thermoelastic bending heat transfer mechanisms was verified by not being possible to fit the phase data to the phase expressions given in Refs. 43-45 for these mechanisms, taking the thermal diffusivity value of \( \alpha_{\text{calc}} = 0.0575 \text{ cm}^2\text{s}^{-1} \) or 0.0825 \text{ cm}^2\text{s}^{-1} as the initial value. On the other hand, the expression for the phase corresponding to nonradiative surface recombination heat transfer mechanism\textsuperscript{43-45} written as

\[
\Phi_{\text{ph}} = \frac{\pi}{2} + \tan^{-1} \left[ \frac{(bD/v)(\omega \tau_{\text{eff}} + 1)}{(bD/v)(1 - \omega \tau_{\text{eff}}) - 1 - (\omega \tau_{\text{eff}})^2} \right]
\]

where \( \tau_{\text{eff}} = \tau(Da - 1) \), \( b = (\pi f/a)^{1/2} \), \( \omega = 2\pi f \), \( a \) is the thermal diffusivity, \( D \) is the carrier diffusion coefficient, \( v \) is the surface recombination velocity and \( \tau \) is the recombination time, was successfully fitted to the \( \Phi_{\text{ph}} \) versus \( f \) plot in the modulation frequency range of 52-70 Hz. From the best fit, values of \( \alpha_{\text{eff}} = 0.07305 \text{ cm}^2\text{s}^{-1}, D = 29.82 \text{ cm}^2\text{s}^{-1}, v = 149.94 \text{ cm}^2\text{s}^{-1} \) and \( \tau = 343.8 \text{ ns} \) were obtained for the thermal diffusivity, carrier diffusion coefficient, surface recombination velocity and recombination time, respectively. The slight reduction in the thermal diffusivity for the annealed sample can be associated with decreasing the crystallite size and volume fraction of SnTe, accompanied by an increase in the volume fraction of SnO\textsubscript{2} and the emergence of a significant volume fraction of elemental Te. The last two phases can behave as phonon scattering centers, thus reducing the phonon free path.

It will be assumed that the measured effective thermal diffusivity \( \alpha \) for as-milled and annealed samples can be described by the Lichtenecker's logarithmic mixture law\textsuperscript{52,53}

\[
\alpha_{\text{eff}} = \sum_{i} \alpha_i \rho_i
\]

where \( n \) is the number of phases and \( \alpha_i \) and \( \rho_i \) are the thermal diffusivity and density of phase \( i \). The values \( \alpha_{\text{calc}} = 0.0575 \text{ cm}^2\text{s}^{-1} \) and \( \alpha_{\text{SnTe}} = 0.3767 \text{ cm}^2\text{s}^{-1} \), respectively. Using the effective thermal diffusivity value of \( \alpha_{\text{eff}} = 0.0825 \text{ cm}^2\text{s}^{-1} \) for the as-milled sample and the relative volume fraction values below, a value of \( \alpha_{\text{SnTe}} = 0.0574 \text{ cm}^2\text{s}^{-1} \) is obtained for the as-milled SnTe phase, while a value of \( \alpha_{\text{SnTe}} = 0.0660 \text{ cm}^2\text{s}^{-1} \) is obtained for the annealed SnTe phase. These values are similar, but slightly larger than the value calculated using the TAPP data \( \alpha_{\text{SnTe}} = 0.0575 \text{ cm}^2\text{s}^{-1} \). Using the high-energy ball milling and hot-pressing techniques, Zhang et al.\textsuperscript{49} produced an undoped SnTe phase and reported a value of \( \alpha_{\text{SnTe}} = 0.056 \text{ cm}^2\text{s}^{-1} \) for the thermal diffusivity at room temperature. This value agrees quite well with those obtained in this study.

The performance of a thermoelectric material can be improved if its thermal conductivity is reduced without strong degradation of the electrical properties. It has been reported that materials having small crystallite size can have larger thermoelectric conversion efficiency due to a decrease in the thermal conductivity of the lattice\textsuperscript{56,57}. In this study, both as-milled and annealed samples have mean crystallite sizes of nanometric dimensions (75.2 nm and 59.3 nm).

According to Tripathi and Bhandari\textsuperscript{58}, the \( \sqrt{E_g/K} \) ratio, where \( E_g \) is the energy gap in eV and \( K \) the thermal conductivity in W/mK, can be used as an initial guide to evaluate the good thermoelectric materials and gives a reasonably good agreement with the maximum value of ZT for these materials. The values of energy gap \( E_g = 0.182 \text{ eV} \) for the as-milled and \( E_g = 0.187 \text{ eV} \) for the annealed samples were obtained from the UV-VIS-NIR measurements; the values of density \( \rho = 6486 \text{ kgm}^{-3} \) for as-milled and \( \rho = 6463 \text{ kgm}^{-3} \) for annealed samples were obtained from the Rietveld refinements of the XRD patterns; the values of thermal diffusivity \( \alpha = 0.0774 \times 10^4 \text{ m}^2\text{s}^{-1} \) for the as-milled and \( 0.0660 \times 10^4 \text{ m}^2\text{s}^{-1} \) for annealed samples were obtained from the PAS measurements.
Considering the value of specific heat given in TAPP software \(28\) for the bulk SnTe phase \((C_p = 211 \text{ J kg}^{-1} \text{ K}^{-1})\), the thermal conductivity \(k = \rho C_p a\) was estimated and the calculated values were 10.59 W m\(^{-1}\) K\(^{-1}\) for the as-milled and 9.00 W m\(^{-1}\) K\(^{-1}\) for annealed samples. These values are slightly larger than that reported by Gelbestein\(^{48}\) of \(k = 7.9\) W m\(^{-1}\) K\(^{-1}\) for bulk SnTe. Values of \(\sqrt{E_g} / K = 0.0403\) for the as-milled and 0.0480 for annealed samples were obtained. Zhang et al.\(^{28}\) considering the value of specific heat given in TAPP software \(8\), Materials Research Laboratory, University of Santa Catarina (LABINC-UFSC) for the optical transmittance measurements.

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