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Sb₂Te₃/graphite nanocomposite: A comprehensive study of thermal conductivity



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ABSTRACT

Thermoelectric performance largely depends on the reduction of lattice thermal conductivity (κ_L). The study of the thermal conductivity (κ) of a Sb₂Te₃/graphite nanocomposite system demonstrates ~40% reduction in κ_L with graphite incorporation. A plausible explanation of intrinsic low κ_L observed in Sb₂Te₃ based system is presented by modeling experimental specific heat (C_p) data. Raman spectroscopy measurement combined to X-Ray diffraction data confirms the presence of graphite as separate phase in the composite sample. It is found that phonon scattering dominates heat transport mechanism in the nanostructured Sb₂Te₃/graphite composite. Large reduction in κ_L is accomplished by intensifying scattering rate of phonons via various sources. Graphite introduces effective scattering sources, *i.e.*, defects of different dimensionalities in synthesized nanocomposite sample. Furthermore, graphite mediates phonon-phonon coupling and enhances lattice anharmonicity, which causes an intrinsic scattering of phonons with all frequencies in the Sb₂Te₃/graphite nanocomposite sample. Dislocation density and phonon anharmonicity of the synthesized samples are estimated from in depth analysis of temperature dependent synchrotron powder diffraction and Raman spectroscopic data. κ_L value as low as 0.8 W m⁻¹K⁻¹ at 300 K, achieved with graphite dispersion in Sb₂Te₃ based composite system makes the present comprehensive study an interesting concept to be developed in thermoelectric materials.

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1. Introduction

Thermoelectric (TE) materials have the potential to play a significant role in converting a part of waste heat to useable electrical energy. Materials with intrinsically low thermal conductivity (κ) are of practical interest [1]. In principle, charge carriers, phonons, photons, excitons, magnons can all contribute to heat transport and thus to κ in a material. But in potential TE materials, κ mostly

consists of electronic part (κ_e) and lattice/phonon part (κ_L) with $\kappa_e < \kappa_L$ [2,3]. Lattice thermal conductivity (κ_L) is the only independent tunable parameter in TE Figure of merit $ZT (= \frac{S^2}{\rho\kappa} T)$ where S , ρ and T are the Seebeck coefficient, electrical resistivity and absolute temperature respectively [4–6]. Hence, reduction in κ_L has been a point of great interest in order to improve the efficiency of TE materials, ZT [3,7–11].

Intensifying phonon scattering, *i.e.*, shortening phonon relaxation time (τ) is a promising strategy for achieving low κ_L . Heat carrying phonons have a broad spectrum of frequencies. Different scattering sources have their own frequency (ω) dependence. Grain boundaries (2D defects) can effectively scatter low-frequency phonons ($\tau_B \propto \omega^0$), high frequency phonons are mostly targeted

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by point defects (OD defects) with $\tau_{PD} \propto \omega^{-4}$ [8,9]. Nano or meso structuring would lead to grain boundary engineering, while alloying has been demonstrated as an effective route for modulating point defect [3,7,12]. On the other hand, dislocation strain fields ($\tau_{DS} \propto \omega^{-1}$) and dislocation cores ($\tau_{DC} \propto \omega^{-3}$) are suitable scattering centers for phonons of mid-frequency (1D defects). Kim et al. demonstrated the role of dislocation arrays formed at grain boundaries in lowering κ_L of $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ [8]. κ_L as low as $0.4 \text{ W m}^{-1}\text{K}^{-1}$ is also reported to be achieved by engineering vacancy induced dislocations within grains of PbSe thermoelectrics [9]. In addition, strong anharmonicity in lattice vibration increases phonon-phonon scattering through Umklapp (τ_U) and normal (τ_N) processes ($\tau_{U,N} \propto \omega^{-2}$), which is helpful to scatter phonons of all frequency [13–15]. All the scattering mechanisms contribute collectively to shorten total phonon relaxation time (τ_{total}) and hence decrease κ_L [8,9].

Many of the recent successes in lowering κ_L and hence increasing TE performance have been achieved through composites [16–19], consisting of TE matrix and nanoscale constituents. Low energy charge carriers get filtered in the nanograin boundaries of the composite leading to increase of S . Newly formed hetero-interfaces of TE matrix and dispersoids scatter phonons more effectively than charge carriers leading to decrease of κ without much compromise to ρ [12,20,21]. There have been reports of κ_L reduction in some well-known TE materials like PbTe, SnTe, SnSe, Bi_2Te_3 through composite route [21–29]. Due to its potential for near room temperature application, Sb_2Te_3 , possessing layered crystal structure, is a popular TE material with intrinsically low κ_L [14,30–32]. Very limited efforts have been made to further lower its κ_L through composite approach [19,33,34]. Lee et al. have reported a low κ_L value of $1.4 \text{ W m}^{-1}\text{K}^{-1}$ in Ag_2Te incorporated Sb_2Te_3 composite [34]. However, despite such attempts, underlying mechanism and effect of different type of material defects on phonon scattering in composite systems is still elusive in nature. It is also noteworthy to mention here that understanding of phonon dynamics and its relation with the lowering of κ_L in composite TE systems, which is absolutely critical for further enhancement of TE performance, remains unexplored so far.

We herein report ~40% decrease of κ_L in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite system as compared to its pristine counterpart and have attempted to investigate the role of phonon dynamics in details. Carbon based materials are effective in phonon blocking [16]. The thermal property of graphite, which possesses layered structure, is highly anisotropic [35,36]. In addition graphite is a light eco-friendly material with high electrical in-plane conductivity, high carrier mobility and excellent mechanical properties [35]. These properties encourage us to choose graphite as a possible dispersoid in the Sb_2Te_3 matrix. Interestingly, in this composite system when the wt% of graphite is lower than 1%, its Seebeck coefficient is keeping an unchanged value as compared to the graphite free analogue [36] which allows to study κ in samples having the same charge carrier concentrations. In the following, we report on the role of graphite addition on scattering phonons of entire frequency spectrum by various scattering sources, viz., point defects (OD defects), dislocation type defects (1D defects), grain boundary and $\text{Sb}_2\text{Te}_3/\text{graphite}$ heterointerfaces (2D defects). Both the microscopic characterization based on temperature-dependent synchrotron radiation diffraction and Raman spectroscopic measurements and macroscopic characterization by specific heat (C_p) measurement of nanostructured $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite system have been performed. Dislocation density in the samples has been calculated by modified Williamson Hall method. Phonon anharmonicity is estimated through temperature dependent synchrotron X-ray, Raman spectroscopic and C_p data. This reveals that anharmonicity arising due to lattice thermal expansion is higher in pristine Sb_2Te_3 sample.

But high phonon-phonon coupling in $\text{Sb}_2\text{Te}_3/\text{graphite}$ ensures an overall increase of phonon anharmonicity in graphite incorporated composite sample. Finally, the obtained clues to low κ_L related to phonon scattering mechanism and anharmonic lattice vibration are discussed.

2. Experiments

To prepare the $\text{Sb}_2\text{Te}_3 + x \text{ wt\%}$ graphite ($x = 0, 0.5$) nanocomposite samples, polycrystalline Sb_2Te_3 ingot was initially synthesized by solid state reaction method [14]. To obtain corresponding $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite samples, desired weight percentage of graphite was added with synthesized Sb_2Te_3 ingots and ball milled, the details of which can be found in supplementary material. Hot pressed pellets of $\text{Sb}_2\text{Te}_3 + x \text{ wt\%}$ graphite samples were used for κ measurement [37]. Low-temperature (15–300 K) powder X-ray Diffraction (XRD) experiments were carried out using the synchrotron radiation facility at Indian beamline BL-18B, Photon Factory, KEK, Japan. X-ray beam of wavelength $\lambda = 0.9782 \text{ \AA}$ was selected for illuminating the samples. For detailed structural characterization, Rietveld refinement of the synchrotron X-ray patterns was performed using MAUD software [38,39]. The microstructural refinement according to the formalism of Popa [40] is capable of modeling both isotropic and anisotropic size and strain broadening. This has been used in the present Rietveld analysis. It is noteworthy to mention that during refinement of $\text{Sb}_2\text{Te}_3 + 0.5 \text{ wt\%}$ graphite sample, no extra texturing effect was required to fit the experimental XRD pattern. The heat capacity C_p measurement was carried out in the temperature range of 2–300 K on Physical Property Measurement System (PPMS) (Model: 6000, Quantum Design, USA) with the heat capacity option that employs relaxation calorimetry. Raman spectroscopy measurements were carried out using a custom built micro-Raman setup [41] employing 532 nm laser as excitation. Samples were mounted in a liquid nitrogen flow cryostat (Linkam make) and the spectra were recorded in the temperature range 80–300 K in backscattering geometry. The details of Raman Spectroscopic measurements can be obtained elsewhere [42].

3. Results and discussion

Phase purity of the synthesized $\text{Sb}_2\text{Te}_3+x \text{ wt\%}$ Graphite ($x = 0, 0.5$) samples is confirmed through X-ray diffraction (XRD). The synchrotron powder diffraction data reveal that both synthesized samples are single phase in nature without presence of impurity phases, at least within the detectable limit of XRD (See Fig. SM1 in supplementary material). No additional peak due to graphite is observed in the XRD data of nanostructured $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite samples. Furthermore, the XRD data indicate a lack of peak shift due to the addition of graphite, which confirms the solid state insolubility of graphite phase in Sb_2Te_3 [21,36]. Thus it can be assumed that graphite is present as separate phase in the present $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite sample. In order to confirm the existence of graphite in $x = 0.5$ sample, Raman spectroscopic study of both samples ($x = 0, 0.5$) are carried out (See Fig. SM2 in supplementary material). It is revealed that Raman active vibrational modes of Sb_2Te_3 , i.e. A_{1g}^1 ($\sim 65 \text{ cm}^{-1}$), E_g^2 ($\sim 119 \text{ cm}^{-1}$) and A_{1g}^2 ($\sim 161 \text{ cm}^{-1}$) are present in both samples, where E_g and A_{1g} modes represent in plane and out of plane vibration respectively (Fig. SM2) [43,44]. The peak around 139 cm^{-1} obtained in both samples can be attributed to the Infra-Red (IR) active mode of Sb_2Te_3 . Presence of similar IR active phonon mode in Raman spectra has also been evidenced earlier [45]. In addition to the peaks associated with the vibrational modes of Sb_2Te_3 obtained in both samples, the Raman

spectra of $x = 0.5$ sample exhibits several Raman-active vibrational modes arising due to graphite. The Raman active modes around 1350, 1580 and 1620 cm^{-1} , as depicted in Fig. SM2 arise due to graphite and can be indexed as D, G and D' band of graphite, respectively [46]. It is noteworthy to mention that G band, signature of sp^2 -hybridized carbon, is one of the most distinct features in Raman spectra of graphitic materials. D, D' band correspond to defect and disorder induced or edge areas of graphite and is generally absent in highly crystalline graphite. In addition, Raman active peak associated with D + G combination mode (2950 cm^{-1}) is also induced by disorder and is a signature of nanostructured graphite. The peak observed at 2700 cm^{-1} arises due to the overtone of D band (2D) of graphite [47]. Thus Raman spectroscopic measurement along with synchrotron XRD data confirm that graphite is present as separate phases in $x = 0.5$ sample and has not entered the unit cell of Sb_2Te_3 .

In order to investigate the role of graphite addition on κ in Sb_2Te_3 , $\kappa(T)$ measurement of the synthesized $\text{Sb}_2\text{Te}_3/\text{graphite}$ composites is performed and presented in Fig. 1(a). The measured κ value ($\sim 1.5 \text{ W m}^{-1}\text{K}^{-1}$) of pristine Sb_2Te_3 at room temperature is in excellent agreement with the earlier reported data [19]. Temperature dependence of κ_L , $\kappa_L(T)$ of both samples are also provided in Fig. 1(b). The details of $\kappa_L(T)$ estimation is provided in the supplementary material [Fig. SM3]. Estimation reveals that κ_e contributes only around 10% of total κ , whereas κ_L dominates κ value, contributing around 90% of total κ for the synthesized samples. Fig. 1(a) and (b) clearly depict that both κ and κ_L values of pristine Sb_2Te_3 decrease by around 40% with graphite addition over the whole temperature range and a low κ_L value of $0.8 \text{ W m}^{-1}\text{K}^{-1}$ at room temperature is obtained in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite sample. The theoretical minimum κ , κ_{\min} for Sb_2Te_3 and related nanocomposites can be estimated using the Cahill-Pohl model [48–50]:

$$\kappa_{\min} = \frac{1}{2.48} n^{2/3} k_B (v_L + 2v_T) \quad (1)$$

where n , v_L , and v_T represent the number density of the atoms, longitudinal and transverse sound velocities, respectively [14,30]. The low κ_L value, experimentally obtained for $x = 0.5$ sample, suggests that graphite incorporation helps to approach estimated κ_{\min} ($\sim 0.31 \text{ W m}^{-1}\text{K}^{-1}$) of Sb_2Te_3 based nanocomposites.

Thermal variation of specific heat, $C_p(T)$ of $\text{Sb}_2\text{Te}_3 + x \text{ wt\%}$ graphite ($x = 0, 0.5$) samples are plotted in Fig. 2. In the temperature range between 200 and 300 K, linear deviation of measured $C_p(T)$ from the Dulong-Petit value, $124.5 \text{ J mol}^{-1}\text{K}^{-1}$ is observed. The deviation between the measured $C_p(T)$ and theoretical value of specific heat at constant volume C_v ($\Delta C_p = C_p - C_v$) increases with graphite addition. ΔC_p per unit K ($\Delta C_p/\text{K}$) changes from $0.015 \pm 0.002 \text{ J mol}^{-1}\text{K}^{-2}$ for $x = 0$ to $0.096 \pm 0.010 \text{ J mol}^{-1}\text{K}^{-2}$ for $x = 0.5$ at 300 K. Estimated $\Delta C_p/\text{K}$ value is of similar order reported earlier for Sb_2Te_3 based system [30]. It is noteworthy to mention that for pristine Sb_2Te_3 , $\Delta C_p/\text{K}$ value does not deviate significantly from the Dulong-Petit value but increases substantially with graphite ($x = 0.5$) incorporation. Such deviation in $C_p(T)$ data ($\Delta C_p/\text{K}$) is a measure of phonon anharmonicity in the system [14,30]. It is reported that phonon anharmonicity helps to scatter phonons and further corroborates with our experimental observation of lower κ (and κ_L) in $x = 0.5$ sample. A simple fitting of the observed $C_p(T)$ data with Debye model, which accounts for the collective motion of phonons, has also been attempted [14,51]:

$$C_p = \gamma T + 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (2)$$

where γT represents electronic contribution, γ is the Sommerfeld coefficient, and $x = hv/k_B T$, $\theta_D = hv_D/k_B$, with θ_D is the Debye temperature, ν_D is the Debye frequency, and R is the gas constant. The best fit values of θ_D ($\sim 160 \text{ K}$), as obtained from the fitting (Solid lines, Fig. 2), agree fairly well with those reported in literature for Sb_2Te_3 based system [14,52]. However, the Debye model (Eq. (2)), fails to adequately reproduce the experimental data in the low temperature regime ($2 \text{ K} \leq T \leq 30 \text{ K}$). The C_p/T^3 vs. T plot (Inset in Fig. 2) of the samples reveals clear deviation from the Debye model below 30 K. The experimental C_p/T^3 vs. T curve for both the samples

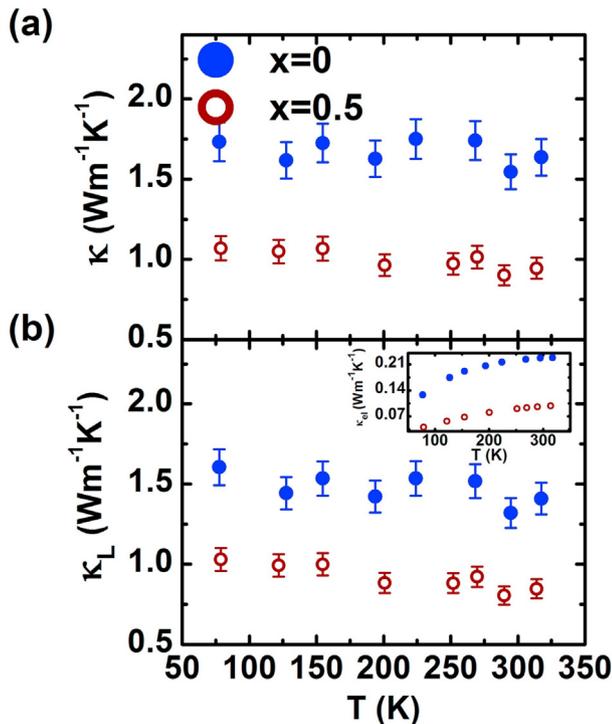


Fig. 1. (Color online) Thermal variation of (a) total thermal conductivity (κ) and (b) lattice thermal conductivity (κ_L) [Inset: electronic part of κ (κ_e)] for $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite samples.

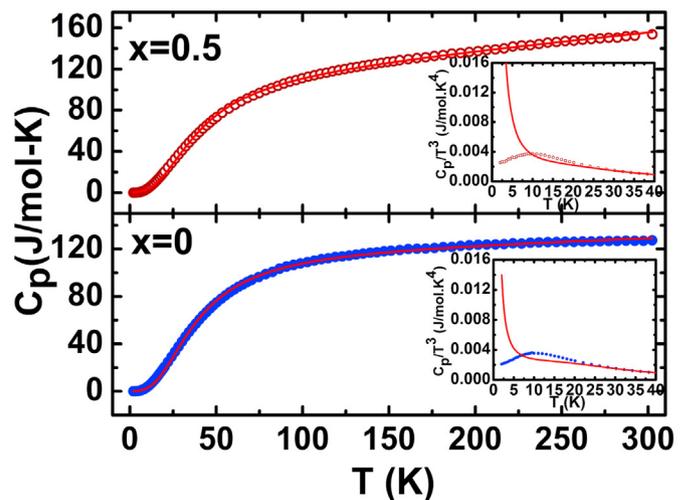


Fig. 2. (Color online) Specific heat at constant pressure (C_p) measured in the range 2–300 K and best fit (red line) to Debye model (Eq. (2)). Inset: C_p/T^3 vs. T plot clearly reveals deviation from the Debye model for $T < 30 \text{ K}$.

depicts a broad peak around 10 K, which Debye model fails to reproduce [Fig. 3(c) and (d)]. Also C_p/T vs. T^2 plot shows non-linear nature for both the samples [Fig. 3(a) and (b)]. Attempts have been made earlier to explain this deviation with the help of Schottky model [14,30,53]. But close observation divulges that Schottky model alone cannot explain the deviation observed in the low temperature $C_p(T)$ data ($T \leq 30$ K) and till date the issue has not been resolved fully. To explain this anomaly, the low temperature $C_p(T)$ data ($2 \text{ K} \leq T \leq 30 \text{ K}$) has been interpreted using a two-level Schottky model superimposed to Debye model with embedded Einstein oscillators [54–56]:

$$\frac{C_p}{T} = \gamma + \beta T^2 + \frac{C_S}{T} \left(\frac{\theta_S}{T} \right)^2 \frac{\exp\left(\frac{\theta_S}{T}\right)}{\left[1 + \exp\left(\frac{\theta_S}{T}\right)\right]^2} + \sum_n \left(A_n (\theta_{E_n})^2 \cdot (T^2)^{-\frac{3}{2}} \cdot \frac{\exp\left(\frac{\theta_{E_n}}{T}\right)}{\left(\exp\left(\frac{\theta_{E_n}}{T}\right) - 1\right)^2} \right) \quad (3)$$

$$\text{with } \beta = C \cdot \frac{12\pi^4 N_A k_B}{5\theta_D^3} \text{ and } C = 1 - \sum_n \frac{A_n}{3NR}$$

where N_A , C_S , θ_S , A_n , θ_{E_n} and N are Avogadro number, Schottky heat capacity prefactor, Schottky temperature, prefactor of n^{th} Einstein oscillator mode, characteristics temperature of n^{th} Einstein oscillator and number of atoms per formula unit, respectively. Whilst the first term (γ) and second term (βT^2) accounts for the electronic contribution and Debye lattice contribution to C_p , the third term represents Schottky contribution and the fourth term denotes the contribution from Einstein oscillator modes [30,55]. The best fit curves (solid lines) demonstrated in Fig. 3, depict the nice fitting of the experimentally obtained C_p/T vs. T^2 and C_p/T^3 vs. T curve for both the samples. It is observed that 3 Einstein modes are required to satisfactorily model the $C_p(T)$ data. The characteristics temperatures of the respective Einstein modes (θ_{E_1} , θ_{E_2} , θ_{E_3}) and

other fitting parameters including θ_S are listed in Table 1. The obtained best fit value of θ_S is in excellent agreement with the literature data [30]. The θ_E values as obtained from the fitting also match fairly well with those reported earlier for Sb_2Te_3 (59 K) [30], Bi_2Te_3 (50 K) [30] and TlInTe_2 (25 K, 45 K and 80 K) [55], where the authors interpreted the $C_p(T)$ data by considering combined Debye–Einstein model. However, the present formalism of Einstein oscillators embedded in a Debye host superimposed with Schottky contribution has not been explicitly applied to model the $C_p(T)$ data of Sb_2Te_3 based system. The broad peak observed in the low temperature regime (~ 10 K) of $C_p(T)$ data for both the samples can be ascribed to the excess phonon density of states (PDOS) resulting from low-lying optical phonon modes [57]. Sb_2Te_3 exhibits layered structure with each layer comprising of quintuple [Te(I)–Sb–Te(II)–Sb–Te(I)] stacks (QLs), where each QL is connected by weak van der Waals force [14]. The quasi-localized low energy optical phonon modes, which arise from these weakly bound atoms are manifested as Einstein oscillators and results in excess contribution to C_p in the low temperature region [55,57]. These low energy optical phonons play an effective role in scattering heat carrying acoustic modes and hinder the thermal transport in the system. So the presence of Einstein oscillator modes is favorable to achieve low κ_L in the present Sb_2Te_3 system. Close observation further reveals that the position of the broad peak (~ 10 K) in the low- T $C_p(T)$ data does not significantly alter with graphite addition. It can thus be commented that graphite addition has very little influence on the modes of

Table 1

Best fit parameters of C_p/T^3 vs. T plot with Eq. (3): Sommerfeld coefficient γ , prefactor for Debye lattice contribution to C_p , β , Schottky temperature θ_S and Einstein temperatures θ_{E_1} , θ_{E_2} and θ_{E_3} .

x	γ ($\text{J mol}^{-1}\text{K}^{-2}$)	β ($\text{J mol}^{-1}\text{K}^{-4}$)	θ_S (K)	θ_{E_1} (K)	θ_{E_2} (K)	θ_{E_3} (K)
0	29.3×10^{-4}	6.7×10^{-4}	28	80	47	15
0.5	4.7×10^{-4}	8.5×10^{-4}	27	65	38	11

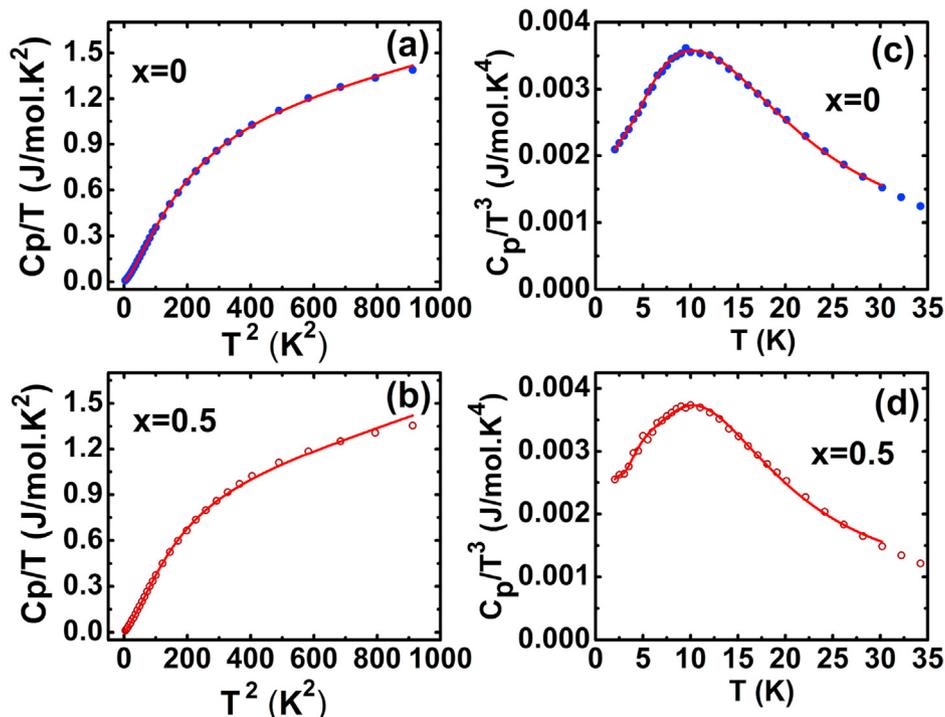


Fig. 3. (Color online) (a), (b) C_p/T vs. T^2 plot and (c), (d) C_p/T^3 vs. T plot for $x = 0, 0.5$ respectively for $2 \text{ K} \leq T \leq 30 \text{ K}$. The red lines represent best fit using two-level Schottky model superimposed to a Debye model with embedded Einstein oscillators (Eq. (3)). It is revealed that at least 3 Einstein oscillators are required to fit the data satisfactorily.

Einstein oscillators as well as on dispersion of the low energy optical phonon modes of $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite system. We present a plausible explanation of intrinsic low κ_L observed in Sb_2Te_3 system based on the indepth analysis and modeling $C_p(T)$ data, hitherto unavailable so far.

Attempt has been made to estimate the dislocation density (N_D) macroscopically for both the samples reported here using the temperature dependent synchrotron XRD data. For estimating N_D , modified Williamson-Hall plot was employed, where the broadening of the XRD peaks are strongly related to N_D and crystallite size via

$$\Delta K = \frac{0.9}{d} + \frac{\pi A^2 B_D^2}{2} N_D^{1/2} K^2 C \pm O(K^4 C^2) \quad (4)$$

The parameter details are provided in the Supplementary materials. From synchrotron powder diffraction the parameters $K [= 2\sin\theta_B/\lambda]$ and $\Delta K [= (\Delta 2\theta_B)\cos\theta_B/\lambda]$ are calculated, where θ_B is the Bragg angle, $\Delta 2\theta_B$ is the Full Width at Half Maximum (FWHM) of the corresponding diffraction peak at θ_B and $\lambda (= 0.09782 \text{ nm})$ is the wavelength of synchrotron X-ray used. N_D is then obtained from the slope of ΔK vs $K^2 C$ curve ($C =$ average dislocation contrast factor). Corresponding plot of the samples for a typical temperature $T = 300 \text{ K}$ is shown in Fig. 4. From Fig. 5, it can be clearly observed that N_D is higher for $x = 0.5$ in the whole temperature range of measurement. Presence of graphite dispersoids as second phase at the grain boundary caused lattice mismatch and generate strain between graphite and the unit cell of Sb_2Te_3 . This promotes enhancement in N_D for the $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite *i.e.*, $x = 0.5$ sample. Similar enhancement in N_D has already been reported for $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and PbTe-PbS TE systems [58,59]. The enhanced dislocations, which are 1D defects, scatter mid-frequency phonons through the dislocation cores and strain [8,9,60] and effectively reduce κ_L in $x = 0.5$ sample. In addition, presence of graphite in the grain boundary regime increases the number of $\text{Sb}_2\text{Te}_3/\text{graphite}$ 2D heterointerfaces, which helps to scatter low frequency phonons [19,21]. In accordance to the recent report of Jin et al., it may be emphasized that to engineer an effective heterointerface optimum size of Sb_2Te_3 nanocrystals is $\sim 10 \text{ nm}$ thickness with uniform hexagonal morphology [61]. Furthermore, graphite also acts as point defects (OD) and significantly contributes in scattering high frequency phonons in $x = 0.5$ sample. Our comprehensive analysis suggests that graphite addition plays a pivotal role in scattering low, mid and high frequency phonons by developing effective 2D (heterointerfaces), 1D (enhanced dislocations) and OD (point defects) scattering sources in $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite sample, thereby lowering κ_L .

Temperature dependent synchrotron powder XRD of both of the

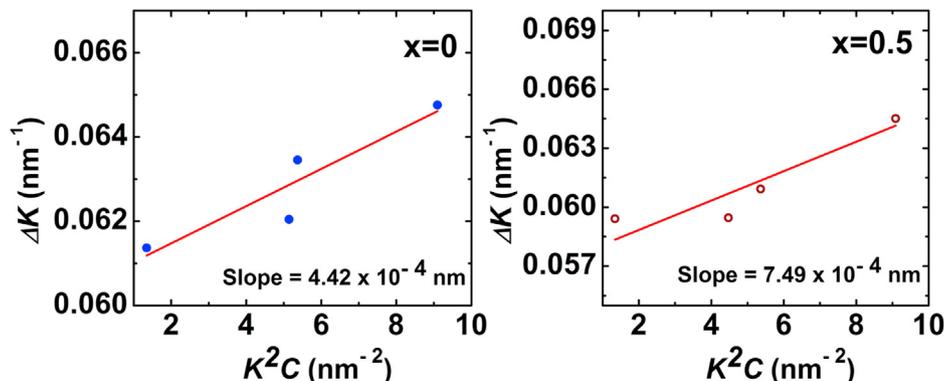


Fig. 4. (Color online) Modified Williamson–Hall plot from synchrotron XRD pattern analysis at a typical temperature $T = 300 \text{ K}$ for the samples indicating larger slope for $x = 0.5$ as compared to $x = 0$.

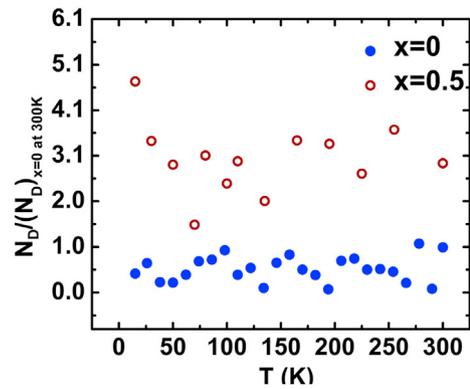


Fig. 5. (Color online) Temperature dependence of ratio of dislocation density (N_D) for the samples calculated using modified Williamson-Hall plot.

$\text{Sb}_2\text{Te}_3 + x \text{ wt\% graphite}$ ($x = 0, 0.5$) was performed in the temperature range $15 \text{ K} \leq T \leq 300 \text{ K}$. The samples retain rhombohedral crystal structure (space group $R\bar{3}m$), with A_7 -type rhombohedral phase until lowest temperature of measurement ($T = 15 \text{ K}$). The diffraction patterns obtained after Rietveld refinement are presented in Supplemental Material. Thermal variation of structural parameters, *i.e.*, a and c of $x = 0$ and 0.5 samples, extracted using Rietveld refinement, is also provided in the supplementary material (Fig. SM4). The refined lattice parameters, *i.e.*, a and c increase monotonically with increasing temperature, indicating usual positive thermal expansion coefficients in both orientations for the synthesized samples. Thermal expansion coefficient is an important parameter, not only for device designing, but also the strain induced due to change in temperature may affect its phonon dynamics [14,30,43,51,62]. So, attempt has been made to study the thermal expansion coefficient in details and explore the corresponding physics towards obtaining better insight about phonon dynamics of the synthesized $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite samples. The linear thermal expansion coefficients α_L are obtained from the derivative, $\alpha_L = \frac{d(\ln L)}{dT}$, of the lattice constants, where L denotes lattice constants a and c . The extracted α_L values are in excellent agreement with the previously reported thermal expansivity data [51,52]. These data appear to be more scattered beyond $\sim 150 \text{ K}$, this anomalous behavior being more pronounced for the $x = 0$ sample. The obtained $\alpha_L(T)$ data is fitted with the Debye model [14,43,51]:

$$\alpha_L(T) = \alpha_0 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (5)$$

where α_0 is a constant and θ_D is the Debye Temperature. $\theta_D = 160$ K, as obtained from the fitting of $C_p(T)$ data with Debye model, is used for fitting the $\alpha_L(T)$ data. Solid lines in Fig. 6 represent the best fit obtained using Debye model. Fig. 6 clearly depicts that below θ_D both α_a and α_c are well fitted by this model. In contrast, above θ_D both the agreement is less obvious as the α_a and α_c experimental values are more scattered. Such deviation of α_L from the Debye model, reported earlier for Sb_2Te_3 related systems, has generally been ascribed to the presence of higher order anharmonic effect in the system [63]. Anomalous behavior of van der Waals forces between Quintuple layers (QL) of Sb_2Te_3 at high temperature could also be a reason for the observed deviation [52]. But departure of both α_a and α_c from Debye model above θ_D consolidates the idea that phonon anharmonicity prevails in the synthesized Sb_2Te_3 based samples discussed here. It is noteworthy to mention that anharmonic lattice vibrations help to reduce κ_L by scattering phonons of all frequency and explains the low κ_L values observed in Sb_2Te_3 based system. However, the role of graphite addition on lattice anharmonicity has been investigated further in order to address the observed 40% reduction of κ_L for $x = 0.5$ sample.

To confirm phonon anharmonicity in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite samples, in-depth temperature dependent Raman spectroscopic study in the range from 300 K to 80 K is carried out. No additional Raman mode other than those appeared at 300 K (discussed above) is observed down to 80 K for both samples. The Raman spectra of both the samples are fitted with Lorentzian function and the extracted temperature dependence of phonon frequency (peak positions, ω) are used for analysis of lattice anharmonicity. Temperature dependent phonon frequency of all the characteristics phonon modes of Sb_2Te_3 i.e., A_{1g}^1 , E_g^2 and A_{1g}^2 , as obtained for both synthesized samples, are plotted in Fig. 7. The phonon frequencies for all the phonon modes soften and broaden with increase of temperature. Such temperature induced hardening and softening have been reported earlier for different materials including Bi_2Te_3 , Bi_2Se_3 , Sb_2Te_3 [14,43,62] and indicate the anharmonic nature of the characteristic phonon modes. The observed temperature dependence of phonon frequency and departure from its bare harmonic value owe mostly to the phonon-phonon coupling in the system. This phonon-phonon coupling renormalizes the phonon energy and lifetime and we get non-zero higher (>2nd) order anharmonic terms from the polynomial expansion of the lattice potential in normal coordinates. To quantify the anharmonic part arising due to phonon-phonon coupling, the simplest approximation is to use symmetrical three phonon coupling model,

also known as Klemens's model [43,64,65]. This model works based on the assumption that an optical phonon decays into two phonons with equal energies and opposite momentum. The model does not take into account the "coalescence" process where two phonons fuse into a third phonon [66]. While this model is successful in describing thermal variation of phonon in some materials [67], more general approach is to use an approximation which also includes anharmonic contributions due to thermal expansion and asymmetric decay into two or more different phonons [68–70]. According to the generalized Klemens's model, the temperature dependence of phonon frequency can be expressed as:

$$\omega(T) = \omega_0 + \Delta\omega^{(1)}(T) + \Delta\omega^{(2)}(T) \quad (6)$$

where ω_0 is bare harmonic frequency; $\Delta\omega^{(1)}(T)$ is the anharmonic correction arising due to the lattice thermal expansion originating from the thermal expansion induced changes in the harmonic force constant. The term $\Delta\omega^{(1)}(T)$ is described as:

$$\Delta\omega^{(1)}(T) = \omega_0 \left[\exp(-\gamma_G) \left[\int_0^T [\alpha_c(T') + 2\alpha_a(T')] dT' - 1 \right] \right] \quad (7)$$

where γ_G is the Grüneisen parameter [14,51]. $\Delta\omega^{(2)}(T)$ is anharmonic phonon-phonon coupling term and is represented by:

$$\Delta\omega^{(2)}(T) = A_1 [1 + n(\omega_1) + n(\omega_2)] \quad (8)$$

with $\omega_1 = \omega_2 = \omega_0/2$ and $n(\omega) = [\exp(h\omega/k_B T) - 1]^{-1}$; where 'A₁' is the fitting parameter.

The best theoretical fit to Klemens's model (Eq. (6)) for the Raman active A_{1g}^1 , E_g^2 and A_{1g}^2 phonon modes of both $x = 0$ and 0.5 samples is represented by individual solid lines in Fig. 7. The obtained best fit values of bare harmonic frequency, ω_0 , for all the characteristics phonon modes are presented in Table 2. It is observed that ω_0 for all the phonon modes increases with graphite addition. At room temperature and 1 atm pressure, pressure coefficients for A_{1g}^1 , E_g^2 and A_{1g}^2 phonon modes are 4.30, 2.11, 2.57 $\text{cm}^{-1} \text{GPa}^{-1}$, respectively [71]. From the observed shift of ω_0 (Table 2), it is further revealed that in $x = 0.5$ sample, graphite provides a large compressive strain to the Sb_2Te_3 matrix [72]. Such strain on the matrix due to graphite incorporation creates dislocation in Sb_2Te_3 [73,74] and corroborates with the XRD analysis which confirms higher dislocation density (N_D) in the $x = 0.5$

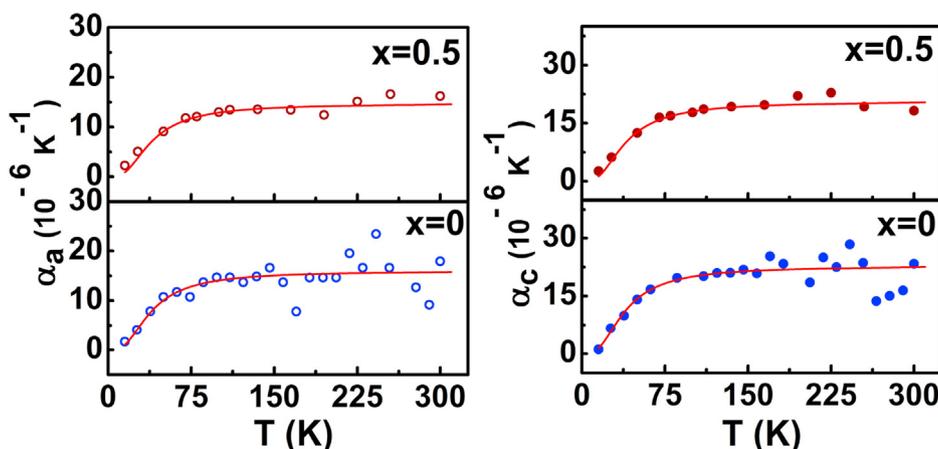


Fig. 6. (Color online) Temperature dependent linear thermal expansion coefficient α_L i.e., α_a and α_c for $x = 0$ and $x = 0.5$. The errors in α_a and α_c are within the size of the data points. Red lines show attempted fitting with Debye model.

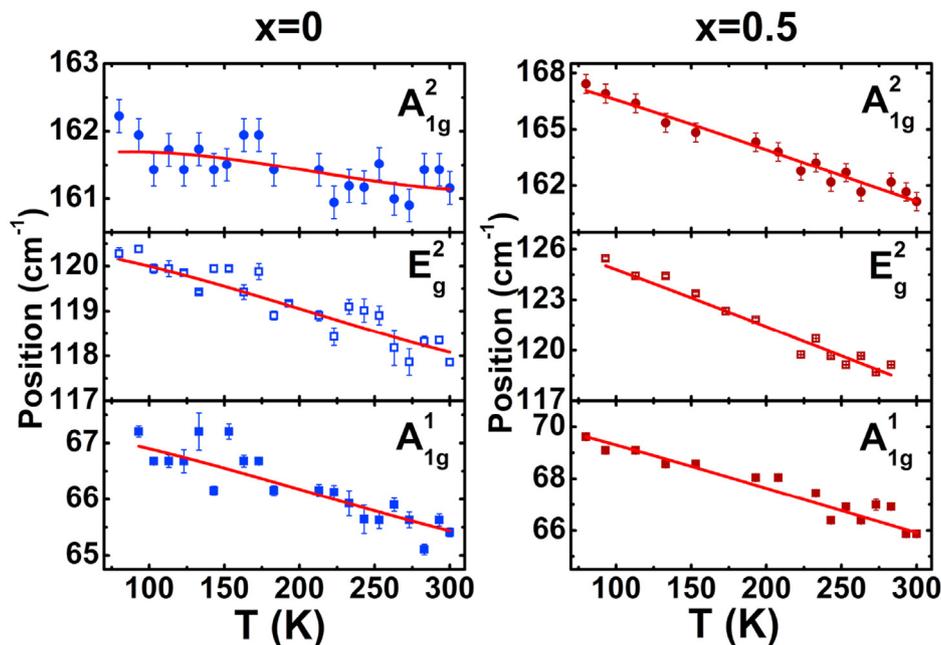


Fig. 7. (Color online) Temperature dependence of the phonon frequency for $\text{Sb}_2\text{Te}_3 + x$ wt% graphite samples showing softening of all modes with increasing temperature. The data has been fitted with Klemens's model (Eq. (6)) to investigate phonon anharmonicity in the samples.

Table 2

Bare harmonic frequency, ω_0 of all the characteristics phonon modes A_{1g}^1, E_g^2 and A_{1g}^2 for $x = 0$ and 0.5 extracted from fitting temperature dependence of phonon frequency with Eq. (6) and additional pressure exerted on Sb_2Te_3 matrix due to addition of graphite in $x = 0.5$ sample.

Raman Mode	ω_0 for $x = 0$ (cm^{-1})	ω_0 for $x = 0.5$ (cm^{-1})	Net pressure due to graphite addition (GPa)
A_{1g}^1	67.39	70.79	0.75
E_g^2	120.53	127.86	2.04
A_{1g}^2	161.40	168.82	2.47

sample. The interfaces between the graphite and main Sb_2Te_3 phase in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite thus introduces lattice strain in the system and plays a beneficial role to the suppression of κ_L [72].

To gain further quantitative insights, we focus on the temperature dependence part of phonon frequency (Eq. (6)). As mentioned above, the anharmonic contribution to phonon vibration comes from two sources: $\Delta\omega(T) = \Delta\omega^{(1)}(T) + \Delta\omega^{(2)}(T)$. Temperature dependence of $\Delta\omega^{(1)}(T)$ and $\Delta\omega^{(2)}(T)$ of all the three characteristics phonon modes A_{1g}^1, E_g^2 and A_{1g}^2 are calculated individually using Eqs. (7) and (8) for both samples and plotted in Fig. 8. Fig. 8(a) reveals that $|\Delta\omega^{(1)}(T)|$ is higher in $x = 0$ sample, i.e., anharmonic contribution from lattice thermal expansion is larger in the pristine sample. The estimated large compressive strain in Sb_2Te_3 matrix affects its harmonic force constant and is reflected in the observed lower anharmonicity of lattice thermal expansion of $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite ($x = 0.5$) sample. The temperature dependent variation of $|\Delta\omega^{(1)}(T) + \Delta\omega^{(2)}(T)|$ for all the characteristics phonon modes of Sb_2Te_3 are plotted in Fig. 9. It is clearly revealed that the phonon-phonon coupling term $|\Delta\omega^{(2)}(T)|$ is much higher in $x = 0.5$ sample (Fig. 8(b)). Furthermore, changes in $|\Delta\omega^{(2)}(T)|$ overwhelms $|\Delta\omega^{(1)}(T)|$, such that the overall anharmonic contribution to phonon vibration, i.e., $|\Delta\omega^{(1)}(T) + \Delta\omega^{(2)}(T)|$ becomes larger in $x = 0.5$ sample (Fig. 9). This high $|\Delta\omega^{(2)}(T)|$ in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite indicates that

graphite acts as a mediator for phonon-phonon coupling and plays a significant role in enhancing the anharmonic contribution to phonon vibration. This higher phonon anharmonicity in graphite contained composite sample helps in suppressing κ_L by scattering phonons of all frequency.

Strong phonon scattering effect is reported to be also effective in $\text{Bi}_2\text{Te}_3/\text{CNT}$ composite system [16,18,61], where heterointerfaces, nanopores and other defects efficiently suppress thermal transport. $\text{Bi}_2\text{Te}_3/\text{SWCNT}$ (Single wall carbon nanotube) based hybrid sample has recently been reported as an excellent route for the design and fabrication of high-performance flexible TE materials [61]. Our results clearly indicate that nanocompositing with graphite, which is also a carbon-based material, is a favorable route for reducing κ_L keeping Seebeck coefficient unchanged. However, it may be acknowledged that such low 0.5 wt % of graphite giving a small molar ratio ($\text{Sb}_2\text{Te}_3:\text{C} = 3.835:1$) is already too high to avoid an increase of the grain boundary resistance and as mentioned in our previous report on $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposites, as far as ZT value is concerned the positive effect in κ_L is subdued by decrease in electrical conductivity with graphite addition [36]. It is noteworthy to mention that in $\text{Sb}_2\text{Te}_3/\text{Ag}_2\text{Te}$ composite, Lee et al. achieved similar κ_L reduction of 50%, but with 35 wt% of Ag_2Te [34]. In the other report of Sb_2Te_3 based composite with PEDOT [33], the thermoelectric properties of the pristine Sb_2Te_3 ($ZT \sim 0.15$ at 300 K) are much lower than those reported by us [36]. In that respect, the present study showing the graphite potentialities should be completed in the future with lower graphite concentration to avoid such drastic electrical conductivity degradation. The approach of

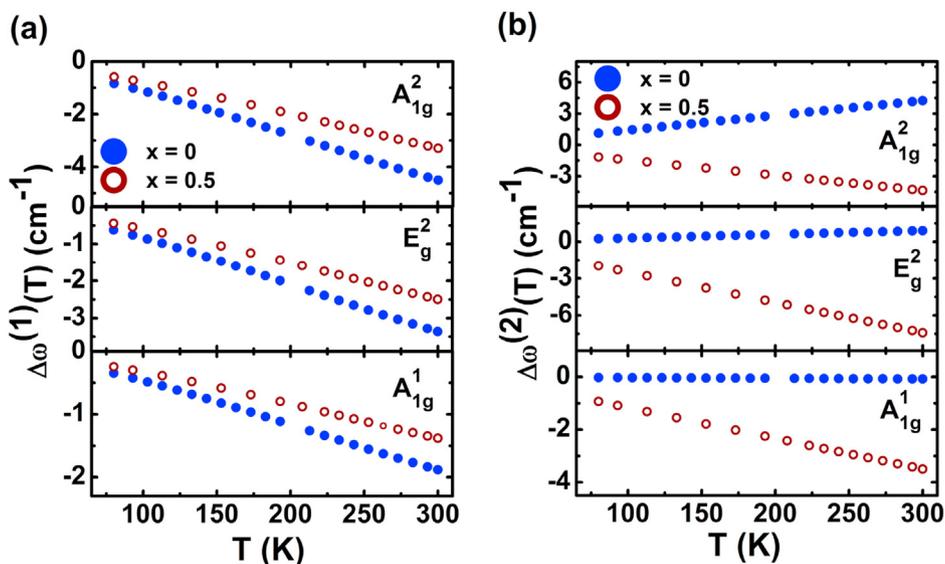


Fig. 8. (Color online) Thermal variation of $\Delta\omega^{(1)}(T)$ and $\Delta\omega^{(2)}(T)$ revealing that anharmonic correction arising due to the lattice thermal expansion is greater for pristine sample while phonon-phonon coupling is higher in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite.

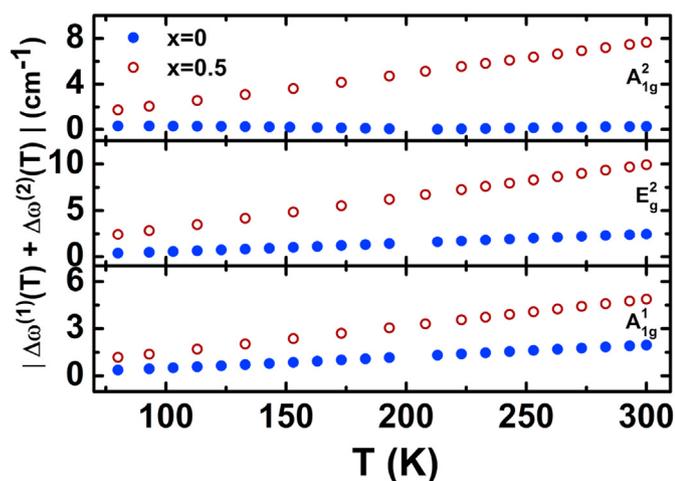


Fig. 9. (Color online) Total anharmonicity present in the samples for the whole temperature range under investigation.

nanocompositing with graphitic materials can be applicable to a series of similar layered TE materials, including Bi_2Te_3 , Bi_2Se_3 and Sb_2Te_3 , and both n - and p -type TE materials can be fabricated using this method [61].

4. Conclusion

Advances in TE materials are intimately related to the reduction of κ_L , the only independent parameter in ZT. In this work, the efficiency of graphite on suppressing κ_L in $\text{Sb}_2\text{Te}_3/\text{graphite}$ nanocomposite system is demonstrated. Graphite effectively contributes in scattering phonons of different length scale and intensifies phonons scattering rate. Dispersion of graphite in Sb_2Te_3 also modulates phonon anharmonicity and enhances scattering of phonons over the entire spectrum. The synergistic role of graphite in $\sim 40\%$ reduction of κ_L value observed in nanostructured $\text{Sb}_2\text{Te}_3/\text{graphite}$ composite system makes the present strategy a possible route to improve TE materials. Thus, nanocompositing with

graphite is worth trying for lower graphite concentration in Sb_2Te_3 and applying to other TE materials.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmat.2020.11.014>.

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