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Graphene Boosts thermoelectric Performance of a Zintl phase Compound

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Abstract:

The concept of nanocomposites derived by incorporating a second minor phase in bulk thermoelectric materials have established itself as an effective paradigm for optimizing the high thermoelectric performance. In this work, this paradigm is for the first time extended to bulk Zintl phase Mg$_3$Sb$_2$ and its isoelectronically Bi-doped derivative Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ system. Herein, we report the synthesis, microstructural details, electronic structure and thermoelectric properties of (Mg$_3$Sb$_2$, Mg$_3$Sb$_{1.8}$Bi$_{0.2}$)/Graphene Nanosheets (GNS) nanocomposites with different mass ratios. Field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) investigation reveals that Mg$_3$Sb$_2$ nanoparticles are homogenously anchored on the surface of GNS. We demonstrate that Mg$_3$Sb$_2$-based materials incorporated with small content of graphene outperform optimally, resulting to a potential p-type thermoelectric materials. The present nanocomposite additive of GNS deriving such a novel nanocomposites of (Mg$_3$Sb$_2$, Mg$_3$Sb$_{1.8}$Bi$_{0.2}$)/GNS, enhances the electrical conductivity significantly, thereby resulting a substantially large increase in the power factor. The enhanced electrical conductivity of these nanocomposites is attributed to the increase in the carrier concentration and high carrier mobility owed to the ultra high mobility of graphene. X-ray photoelectron spectroscopy (XPS) core level spectra confirm weak bonding between GNS and Mg$_3$Sb$_2$. Increase in carrier concentration is reflected in XPS valence band spectra and change in spectral weight near valence band maxima is indicative of increased electrical conductivity in the nanocomposite material. The thermal conductivity of these nanocomposites is noted to be reduced at high temperature. These favorable conditions lead to enhanced thermoelectric figure-of-merit (ZT) ≈ 0.71 at 773K for Mg$_3$Sb$_2$/GNS and a ZT ≈ 1.35 at 773 K for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS nanocomposites with the mass ratio of 80:1 which are ~170% and ~125% higher values compared to bare Mg$_3$Sb$_2$ and bare Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ respectively. We strongly believe that the present novel strategy of
fabricating such nanocomposite of Zintl compound by utilizing, GNS, as a nanocomposite additive, may provide an emerging path for improving thermoelectric properties of various Zintl phase compounds.

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Introduction

The prospects of climate change, eventual fossil fuel depletion and increasing CO$_2$ content, revive tremendous interest in exploring thermoelectric materials with high efficiency by which a heat-to-electricity energy conversion could be accomplished. The efficiency of thermoelectric energy conversion depends on material’s dimensionless figure of merit ZT, defined as $ZT = \frac{\alpha^2 \sigma T}{\kappa}$ where $\sigma$ is the electrical conductivity, $\alpha$, Seebeck coefficient, $\kappa$, the thermal conductivity and $T$, the absolute temperature. An efficient thermoelectric material requires high $\alpha$ and $\sigma$ and hence large power factor (PF= $\alpha^2 \sigma$ ) as well as a low value of $\kappa$. A large value of power factor of a material requires to possess large effective mass ($m^*$) and high carrier mobility $\mu$.

Several strategies such as doping, solid solution alloying, and nanostructuring-nanocomposite, have been utilized to modify the structure, hence improving the thermoelectric properties. Such microstructural modifications lead to several important mechanisms e.g. shifting of the Fermi level, creating local band resonant states, facilitating the convergence of valence band or conduction bands, inducing high effective mass and interface energy filtering effect which is usually helpful to improve the electronic properties. Apart from the improvement of electronic properties, these strategies are also helpful to impede the propagation of thermal phonons by enhancing interface phonon scattering together with creating local structural disorder to increase the frequency of phonon scattering processes as well. Based on these strategies many materials such as Bi$_2$Te$_3$, LAST, TAGS, PbTe, SiGe and Zintl phase compounds have been widely investigated and high ZT had been optimized.

All of the above strategies were mainly focused on increasing the $m^*$ and reducing the lattice thermal conductivity. Unfortunately, the possibility to improve the carrier mobility ($\mu$)
was missed by the researchers which had been largely the victim of such structural modifications and hence needs to be focused for further improvement in thermoelectric properties.

Along the prospective to improve the electrical properties, graphene with high carrier mobility (µ) can be utilized as composite additive for thermoelectric matrix in order to improve the thermoelectric performance of resulting nanocomposites. Graphene has become one of the most exciting material due to its unique electrical, optical, opto-electronics, and mechanical properties. Graphene, particularly, with its two dimension (2D) single layer structure and with sp² hybridization exhibits several intriguing properties e.g. high electrical conductivity (≈ 6,000 Scm⁻¹) high carrier mobility, (≈ 20,000cm²V⁻¹s⁻¹) high specific surface area, (≈ 2600m²g⁻¹) and excellent mechanical properties (mechanical stiffness ≈ 130GPa).⁵⁰⁻⁵⁶ These exciting features of graphene make them a promising candidate for developing various kinds of functional nanocomposites with potential applications in super capacitors⁵⁷,⁵⁸, electric circuit⁵⁹, fuel cell⁶⁰, conductive polymers⁶¹ and bio-sensors⁶². Interestingly, it has been argued by some researchers that the addition of graphene in Ag-matrix could increase the electrical conductivity by introducing large number of electronic transmission channels.⁶³ However, till date; only few reports⁶⁴⁻⁶⁸ are available where graphene has been utilized as inclusions in thermoelectric materials for optimizing their high ZT.

On the other hand, Zintl phases are considered as an unique class of thermoelectric materials due to their unusual structural characteristics which lead to an important behavior of phonon–glass electron–crystal (PGEC)⁶⁹ needed for a materials to achieve high ZT.⁷⁰,⁷¹ They combine distinct regions of covalent bonding ideal for electron–crystal properties and ionically bond cations that can be easily be substituted for precise tuning of electronic properties, leading to the desired “electron crystal” behavior.⁷⁰,⁷² The complex structures create phonon–glass properties resulting in low lattice thermal conductivity, making many Zintl compounds a natural “phonon glass”.⁷³,⁷⁴ As a consequences of these behaviors, a varieties of Zintl phase compounds such as Yb₄MnSb₁₁,³⁵ Zn₄Sb₃,³⁶ Yb₉Mn₄₂Sb₉,³⁷ filled skutterudites,³⁸,³⁹ clathrates,⁴⁰,⁴¹ (Yb,Ba)Zn₂Sb₂,⁴²,⁴³ YbCd₂Sb₂,⁴⁴ BaGa₂Sb₂,⁴⁵ (Eu₅,Yb₅)In₂Sb₆,⁴⁶,⁴⁷ EuZn₂Sb₂,⁴⁸ AZn₂Sb₂⁴⁹ etc. with high ZT have been developed. However, the use of expensive rare earth elements and toxic chalcogenides in majority of Zintl phase materials limits their use in large scale industrial application for power generation.
Mg$_3$Sb$_2$ is a unique Zintl phase compound constituted with cheap, rare earth free and non-toxic constituents which crystallizes in cubic bixbyite ($\alpha$-phase) as well as in hexagonal structures ($\beta$-phase).\cite{4} The $\alpha$-phase cubic bixbyite structure is La$_2$O$_3$–type which is the high temperature phase, structured with 80 atoms per unit cell with 48 Mg and 32 Sb atoms. At low temperature, below ~1200K, Mg$_3$Sb$_2$ crystallizes to Mn$_2$O$_3$ type $\beta$-phase with unit cell composed of 5 atoms (3 Mg and 2 Sb). The $\beta$-phase hexagonal structure (Space group P$\overline{3}$ml; No. 164) which is under our investigation, consists of two inequivalent Mg sites, denoted as Mg(I) and Mg(II) which are covalent and ionic in nature respectively. Thus, the bonding characteristic of Mg$_3$Sb$_2$ is in between metallic and ionic.\cite{76,77} Similar to the structure of CaAl$_2$Si$_2$, the stoichiometric Mg$_3$Sb$_2$ compound consists of interspersed Mg$_2$Sb$_2$$^{2-}$ layers (the tetrahedral position in the lattice) and Mg$^{2+}$ cation layers (the octahedral position in the lattice).\cite{78} The $\beta$-Mg$_3$Sb$_2$ phase exhibits a band gap of 0.4 eV. It has a fairly large effective mass, high thermopower, low thermal conductivity but unfortunately a poor electrical conductivity which is largely the reason for the low thermoelectric performance. In our earlier report\cite{8}, we demonstrated the increase in ZT in Mg$_3$Sb$_2$$_{2-x}$Bi$_x$ ($0 \leq x \leq 0.4$) alloys by isoelectronic substitution of Bi$^{3+}$ on Sb$^{3-}$ site. The enhancement in ZT was attributed to the increased Seebeck coefficient and reduced thermal conductivity. Despite the large increase in the Seebeck coefficient and significant reduction in the thermal conductivity, there was no significant improvement in the electrical conductivity resulting to only moderate improvement in ZT of these materials.\cite{8}

In this work, we have adopted nanocomposite approach by incorporating graphene nanosheet (GNS), in Mg$_3$Sb$_2$ (with high m* and low κ) for further improving the ZT of this potential thermoelectric material. Combination of higher $\mu$ and lower κ would be important to attain superior thermoelectric performance. Several exciting features of graphene namely high electrical conductivity and a large carrier mobility perceived with potential Mg$_3$Sb$_2$ thermoelectric materials may be expected to result in large increase in the electrical conductivity with less effect on the Seebeck coefficient of Mg$_3$Sb$_2$/GNS nanocomposite which is expected to improve the thermoelectric properties.

Herein, we have synthesized Mg$_3$Sb$_2$/GNS nanocomposite by incorporating GNS in different weight fractions in a precursor of pre-synthesized Mg$_3$Sb$_2$ host compound via wet ball
milling route followed by rapid-heating using spark plasma sintering (SPS). An enhanced thermoelectric figure-of-merit (ZT) \( \approx 0.71 \) at 773 K of Mg\(_3\)Sb\(_2\)/GNS with mass ratio of 80:1 for nanocomposite was realized which is about 170\% higher than that of its bulk counterpart Mg\(_3\)Sb\(_2\) compound. Further, the same strategy of fabricating the nanocomposite by incorporating GNS with the same mass ratio of 80:1 was demonstrated in Mg\(_3\)Sb\(_{1.8}\)Bi\(_{0.2}\) and thermoelectric properties were investigated. Interestingly, GNS addition consistently enhances the electrical conductivity (>650\%) which in turn increases the power factor (~90\%) and thereby resulting to a large increase in ZT \( \approx 1.35 \) at 773K of Mg\(_3\)Sb\(_{1.8}\)Bi\(_{0.2}\)/GNS nanocomposite with mass ratio of 80:1. To the best of our knowledge, such strategy of incorporating GNS in Zintl phase thermoelectric matrix for achieving high thermoelectric figure of merit has not been reported so far.

2.0. Experimental Detail

2.1 Materials Processing and Densification

Stoichiometry of Mg\(_3\)Sb\(_2\) and Mg\(_3\)Sb\(_{1.8}\)Bi\(_{0.2}\) with high purity elements magnesium (Mg; 99.99\%, Alfa Aesar), antimony (Sb; 99.99\%, Alfa Aesar), and bismuth (Bi; 99.99\%, Alfa Aesar), were blended by mechanical milling and subsequently grounded in an agate mortar. The blended powders were then subjected to spark plasma sintering (SPS) at a temperature and pressure of 1073 K and 50 MPa, respectively, for a holding time of 10 min. Pellets of 12.7 mm in diameter were obtained. The strategy to following the SPS synthesis route is to melt the stoichiometric at high temperature and cool it fast to form nanosized grains of single Mg\(_3\)Sb\(_2\) composition phase.

The graphite intercalated compound was thermally expanded to get fully thermally expanded graphite\(^7\). The thermally expanded graphite and organic solvent dimethyl formamide (DMF) was taken in the ratio of 5.0 mg/ml and was placed into a stainless steel jar containing stainless steel balls of diameter 5 mm. The ratio of expanded graphite to stainless steel ball was 1:100 by weight. The milling was carried out in an ambient temperature. The mixture was milled by planetary ball milling for 15 hours at a rotation speed 300 rpm. The resulting solution was dried and few layer graphene (FLG) nano sheets (GNS) in the form of powder were obtained\(^8\). The FLG nano sheets derived from the ball milling of expanded graphite in organic solvent was used as conducting reinforcement in the pre-synthesized precursor of Mg\(_3\)Sb\(_2\). Before mixing of
graphene in Mg$_3$Sb$_2$ matrix, it was ball milled for two hours to disperse the GNS properly. The different mass ratio 100:1, 80:1, 60:1 and 40:1 of Mg$_3$Sb$_2$/GNS were mixed in wet ball milling in organic solvent and subsequently the organic solvent was evaporated completely. The resulting mixtures of Mg$_3$Sb$_2$ and GNS were subjected to SPS at temperature of 600 °C and pressure of 50 MPa in order to have a pellet of high density nanocomposite materials. The similar synthesis procedure was followed for fabricating Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS nanocomposite with mass ratio of 80:1.

2.2 Structural Characterization

The gross structural characterization of Mg$_3$Sb$_2$/GNS nanocomposite was carried out by powder X-ray diffractometer (Rigaku Mini Flex II) in reflection θ- 2θ geometry, with position sensitive detector (Ultafast D Tex), operating at 30 kV and 20 mA, using a graphite monochromator and CuK$_\alpha$ radiation with wavelength $\lambda \approx 1.5406$ Å along with CuK$_{\alpha2}$ filter and rotating anode equipped with powder 2θ diffractometer ranging from 20 to 80 degrees. The experimental conditions and parameters such as sample size, power ratings of X-ray tube (30 kV, 20 mA) and other diffractometer parameters such as scan speed, counting steps etc. were kept constant for all diffraction experiments.

The microstructure investigation of host Mg$_3$Sb$_2$ Zintl compound and Mg$_3$Sb$_2$/GNS nanocomposite after SPSed was carried out by field emission scanning electron microscopy (FE-SEM; Model: SUPRA40 VP, operating at 30kV) and HRTEM (Modell: Technai G$^2$F30;STWIN) operating at 300 kV. The elemental analysis of the samples was performed using energy dispersive spectroscopy (EDS) attached to the FE-SEM. The detail of TEM specimen preparation of Mg$_3$Sb$_2$ has been described elsewhere$^8$ and same procedure has been followed for present nanocomposites.

2.3 Thermoelectric Properties

Thermal diffusivity of (Mg$_3$Sb$_2$, Mg$_3$Sb$_{1.8}$Bi$_{0.2}$)/GNS nanocomposite samples were measured by using a laser flash system (Linseis, LFA 1000) on disk-shaped thin specimens with approximate thickness of 1.5 mm and diameter of 12.7 mm. The disc specimens used for thermal diffusivity were sprayed with a layer of graphite in order to minimize errors due to emissivity. Specific heat
was determined by a differential scanning calorimetry (DSC) instrument (822e Mettler Toledo). The thermal conductivity of nanocomposites was calculated using the relation, \( \kappa = d \times C_p \times \rho \) where \( d \) is the thermal diffusivity, \( \rho \) the geometrical pellet density and \( C_p \) the heat capacity. The Seebeck coefficients and the resistivity were measured simultaneously employing commercial equipment (ULVAC, ZEM3) over the temperature range of 300 K to 773 K on samples of polished bars of about \( 3 \times 1.5 \times 10 \text{ mm}^3 \).

2.4. Raman Spectroscopy

The graphene derived from expanded graphite and Mg$_3$Sb$_2$/GNS nanocomposites was characterized by Raman spectrometer (Reninshaw, micro Raman model in Via Reflex) with 514 nm laser excitation and notch filter cutting at 50 cm$^{-1}$ at room temperature. The Raman spectra was recorded from 50 cm$^{-1}$ to 3000 cm$^{-1}$ with 5 mW laser power and 10s exposure time. The 50X microscope objective was used and the spot size of the laser was 1-2 \( \mu \text{m} \).

2.5. Hall measurement

Room temperature Hall Effect was carried out using the van der Pauw method. The Hall coefficient was determined using an a.c. power supply of 29 Hz frequency and magnetic induction of 0.9 T. The Hall carrier concentration \( n_H \) was calculated via \( n_H = 1/eR_H \), where \( R_H \) is the Hall coefficient and \( e \) is the electron charge. The Hall mobility \( \mu_H \) was calculated by a relation \( \mu_H = \sigma/n_He \), where \( \sigma \) is the electrical conductivity.

2.6. Thermal Expansion measurement

The coefficient of thermal expansion (CTE) of GNS, Mg$_3$Sb$_2$, Mg$_3$Sb$_2$/GNS nanocomposites was measured by thermo-mechanical analyzer (TMA-Q400, TA Instruments) in Nitrogen atmosphere in the temperature range 50-500 °C@10 °C /min.

2.7. X-Ray Photo Electron Spectroscopy (XPS)

XPS experiments were carried out in a multi-chamber equipped with an Omicron EA 125 electron energy analyzer and monochromated Al K$_\alpha$ X-ray source with ultra high vacuum (UHV) surface science system maintained at the base pressure of \( 10^{-10} \text{ mbar} \) range. All binding energies
have been referenced to the Fermi edge of an Ar$^+$ sputtered clean polycrystalline Ag sample. The XPS data has been collected using 20 eV analyzer pass energy which results in an overall energy resolution of 0.37 eV determined from the Fermi edge broadening of polycrystalline Ag. The composition of the samples have been determined from the normalized area under the curve of Mg 2s and Sb 4d core levels of Mg$_3$Sb$_2$ and Mg 2s, Sb 4d, and graphene core levels for Mg$_3$Sb$_2$/GNS nanocomposite. These spectra are recorded under similar conditions, i.e. comparable analyzer settings, x-ray source intensity and sample position. Area under the curve of each core level used in composition calculation was normalized by respective photoemission cross section, inelastic mean free path and analyzer transmission function.

3. Results and Discussion

The X-ray diffraction (XRD) pattern of the SPSed pellets of Mg$_3$Sb$_2$, (Mg$_3$Sb$_2$, Mg$_3$Sb$_{1.8}$Bi$_{0.2}$)/GNS nanocomposites are shown in Figure 1(a).

In case of bare Mg$_3$Sb$_2$ compound, all the peaks are well indexed to β-Mg$_3$Sb$_2$ (hexagonal; space group P -3m1, JCPDS no. 00-003-0375) with no detectable impurities of other phases (The inset shows the crystal structure of Mg$_3$Sb$_2$). On the other hand, XRD of all the nanocomposites reveal the presence of graphene peak (at $2\theta \approx 26.51^\circ$) along with prominent peaks of β-Mg$_3$Sb$_2$. The intensity of graphene peaks increases consistently with increasing concentration of GNS in the Mg$_3$Sb$_2$. Fig 1 (b) displays TEM images of GNS revealing the GNS width to be about ~260 nm. The inset of fig. 1(b) is XRD pattern of GNS showing peaks of graphene. No any impurity phase was detected. The HRTEM images obtained from graphene [fig. 1(c)] clearly reveals the lattice fringes corresponding to graphene.\footnote{81}

Figure 2 shows the Raman spectra of GNS, Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposite for mass ratio 80:1. The Raman spectra recorded from graphene reveals three bands at 1354, 1582 and 2723 cm$^{-1}$ corresponding to the disordered (D) band, graphitic (G) band and broad 2D band respectively. The disordered (D) band is due to the sp$^3$ bonding of carbon atoms, graphitic (G) band is due to the sp$^2$ bonding of carbon atoms and broad 2D band which is the second order of the D peak but it is not related to defect level in the structure. The intensity ratio of 2D/G is ~0.50 which corresponds to four to five layers in the graphene. However, for the Mg$_3$Sb$_2$:GNS
nanocomposite with mass ratio 80:1, same Raman shift D, G and 2D peaks are appearing with 2D/G ratio of ~0.50 together with spectra consisting of peak at 114 and 156 cm\(^{-1}\) which corresponds to Mg\(_3\)Sb\(_2\). Thus, the peaks of graphene and Mg\(_3\)Sb\(_2\) for nanocomposites indicate that both phases coexist. The Raman spectra of bare Mg\(_3\)Sb\(_2\) (as shown in inset; fig. 2) consists of only two peaks at 118 and 147 cm\(^{-1}\). However, in case of nanocomposite Mg\(_3\)Sb\(_2\)/GNS (80:1), there is a little shift to the lower side as compared the Raman shifts of Mg\(_3\)Sb\(_2\). This is due to the coexistence of Mg\(_3\)Sb\(_2\) and GNS in the nanocomposite. It can be noted that the Raman spectra only provide the statistical average of the powder sample, where a huge number of graphene sheets in single-, double- or few layered forms coexist. Thus, graphene can be distinguished as three different layers such as single, double, and few layers in more generalized way as suggested by Geim et al.\(^{82}\) and hence practically the graphene in Mg\(_3\)Sb\(_2\)/GNS nanocomposite can be regarded as “graphene” in the form of few layered.

The coefficient of thermal expansion (CTE) can give the idea of dimensional changes occurred in nanocomposites with increasing temperature at defined load. It also gives the idea of bonding between the reinforcing constituent in the nanocomposites. The linear CTEs of the GNS, Mg\(_3\)Sb\(_2\) and Mg\(_3\)Sb\(_2\)/GNS nanocomposites pellets were measured in the temperature range 50-500\(^\circ\)C. A high value of CTE of 310.5 \times 10^{-6} \degree C^{-1} in case of GNS pellet was observed, which is due to poor bonding between the few layer graphene suggesting a linear shrinkage in the pellet with increasing temperature and as a consequence thermal stresses exert on the few layer graphene. On the other hand, in case of matrix Mg\(_3\)Sb\(_2\) a reasonably small value of CTE \approx 18.96 \times 10^{-6} \degree C^{-1} was revealed resulting a strong bonding between constituent which arrest the shrinkage with increasing temperature. Interestingly, in case of Mg\(_3\)Sb\(_2\)/GNS nanocomposites, the CTE \approx 23.46 \times 10^{-6} \degree C^{-1} was observed, which is slightly larger than the CTE of the bare Mg\(_3\)Sb\(_2\) matrix indicating a weak bonding between GNS and Mg\(_3\)Sb\(_2\).

We have earlier reported the detailed electronic structure study of bare Mg\(_3\)Sb\(_2\) using XPS core level and valence band spectra.\(^{8}\) Here, we have employed the XPS to compare the electronic structure of bare Mg\(_3\)Sb and Mg\(_3\)Sb\(_2\)/GNS nanocomposites. Figure 3 show XPS survey spectra of bare Mg\(_3\)Sb\(_2\), GNS and Mg\(_3\)Sb\(_2\)/GNS nanocomposites over wide binding energy (BE) range. Spectrum of GNS (bottom) shows the presence of only carbon related features and absence of O
1s and any other feature verifies the purity of GNS. It can be noted that finite amount of O 1s signal in XPS survey spectrum of GNS has been reported in several recent reports of GNS synthesis using different routes. Usually GNS samples are obtained by the reduction of graphite oxide (GO) and it is not always possible to reduce the attached oxygen functional group completely which is detrimental to the electrical properties of graphene. However, in our case, almost complete absence of O 1s signal indicates the effectiveness of used synthesis procedure in removing oxygen functional group.

Survey spectrum of bare Mg$_3$Sb$_2$ (top) also confirms the purity of the materials as we only see the Mg and Sb related features. We clearly observe the emergence of C 1s signal in the Mg$_3$Sb$_2$/GNS nanocomposites. The C 1s signal increases with increasing mass ratio of GNS which is the evidence of increasing inclusion of GNS in the nanocomposite samples for larger mass ratio of GNS. We have observed the inclusion of GNS in all nanocomposite samples reported here by the presence of C 1s signal (spectra not shown here). We have mainly focused our XPS analysis on Mg$_3$Sb$_2$/GNS (80:1) sample as it performs best among other nanocomposites reported here.

We have acquired the high resolution C 1s XPS core level spectra to confirm the quality of GNS and to identify the presence of any other functional group attached with it. C 1s core level for GNS has been fitted using six Gaussian-Lorentzian components using a least $\chi^2$ iterative program after Shirley background subtraction (Fig. 4, bottom spectra).

The individual deconvoluted components (shaded region) correspond to different functional groups attached with C as identified in the Fig. 4 (graphitic sp$^2$ C=C at 284.55 eV, sp$^3$ C-C at 284.95 eV, C-O at 286.2 eV, C=O at 287.3 eV, O-C=O at 288.6 eV and $\pi-\pi^*$ shakeup feature at 290.5 eV BE). Relative percentages of C=C, C-C, C-O, C=O, O-C=O are found to be 56, 29, 10, 4 and 1 respectively. Experimental uncertainty in BE position is 0.05 eV and ±5% of base value for determining the percentage. Full width at half maximum (FWHM) of C=C component turns out to be 0.6 eV and it varies between 1 – 1.15 eV for other C-functional group components. Energy position and FWHM of sp$^2$ C=C and other components is in good agreement with earlier reports based on the analysis of C 1s of a few layer graphene (FLG) and GNS. Presence of dominating sp$^2$ C=C establishes the graphene nature of our GNS.
Similar fitting routine as of GNS has been applied to C 1s core level spectrum of Mg$_3$Sb$_2$/GNS (80:1). It is clearly evident from nanocomposite material related C 1s fitting that graphene nature of GNS is preserved in nanocomposite Mg$_3$Sb$_2$/GNS (80:1). We observe slight increase in C-C/C-OH component in Mg$_3$Sb$_2$/GNS (80:1) compared to GNS and it could be attributed to the synthesis procedure of nanocomposites (wet chemical synthesis followed by further milling and SPS).

The Mg 1s and Sb 3d core level spectra for bare Mg$_3$Sb$_2$ and nanocomposite Mg$_3$Sb$_2$/GNS (80:1) are shown in figure 5. We do not observe any appreciable change in the BE position and line shape of core levels between bare and nanocomposite samples. It suggests that bonding between GNS and Mg and Sb is either nonexistent or very weak. This observation is also in good agreement with our thermal expansion measurements which suggest loose bonding between GNS and Mg$_3$Sb$_2$.

We have compared the XPS valence band (VB) spectra of bare Mg$_3$Sb$_2$ and nanocomposite Mg$_3$Sb$_2$/GNS (80:1) as presented in Fig. 6. The VB is composed of mainly two features; main peak around 2 eV BE and another peak at around 4.6 eV BE. These peaks are made up of Sb 5p states hybridized with Mg 3s states with dominant character of Sb 5p.\(^8\) No significant change in energy positions or relative intensities of main features is observed between bare and composite material which also confirms the weak chemical interaction between Mg$_3$Sb$_2$ and GNS as observed in core level spectra (Fig. 5). Near $E_F$ energy region is shown in inset of Fig. 6. We have determined the position of valence band maxima (VBM) from the cross-section of two straight line fits.\(^8\) We observe the small change in the BE position of VBM between bare Mg$_3$Sb$_2$ (0.4 eV) and nanocomposite Mg$_3$Sb$_2$/GNS (0.34 eV) with mass ratio 80:1 due to increase in p-type carriers in composite compared to bare Mg$_3$Sb$_2$. We also observe the small increase in the spectral weight near VBM (shown as patterned part) for composite material compared to bare Mg$_3$Sb$_2$ and it may be related to the increased electrical conductivity in Mg$_3$Sb$_2$/GNS nanocomposite.

In order to confirm the phase purity at macroscopic scale, homogeneities and compositional analysis of SPSed pellet of bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites samples were performed by FE-SEM and HRTEM. The homogeneities of SPSed samples in bare Mg$_3$Sb$_2$ and
Mg₃Sb₂/GNS nanocomposites for mass ratios 100:1; 80:1, 60:1 and 40:1 were assessed by averaging the compositions obtained by energy dispersive x-ray analysis (EDAX) at 5 different regions of each sample. The average value of composition is shown in table 1 marked as SEM-EDAX compositions. All the samples were found to be macroscopically homogeneous as revealed by SEM-EDAX analysis given in table 1. Figure 7 shows FE-SEM morphologies of bare Mg₃Sb₂ and Mg₃Sb₂/GNS nanocomposite with mass ratio 80:1.

The SEM image of SPSed bare Mg₃Sb₂ (Fig 7a) sample clearly reveals the homogeneous polycrystalline grains. Energy dispersive X-ray spectrum shown in Fig 7(b) qualitatively reveals the presence of Mg and Sb without any minor impurities. The quantification data obtained from EDAX results to the composition of Mg₃Sb₂ phase. Figure 7(c-f) display FE-SEM morphologies of SPSed Mg₃Sb₂/GNS nanocomposite sample with mass ratio 80:1. The Mg₃Sb₂ particles appear to be uniformly confined on the surface of GNS as shown in Fig 7(c). It is interesting to note that the Mg₃Sb₂ particles in the nanocomposite sample (the particle size ranging from 2.0 nm to 50 nm) are significantly smaller than the particles in bare Mg₃Sb₂ (the particle size ranging from 100 nm to 500 nm). In order to see the consistent behavior of graphene introduction on reducing the size of Mg₃Sb₂ particle, SEM measurements were conducted on all the nanocomposites with mass ratio 100:1, 60:1 and 40:1 which are shown in supplementary information S1. All of the nanocomposite samples show smaller particle size of Mg₃Sb₂ and decreases with increasing GNS concentration. Thus, we believe that graphene refined the size of Mg₃Sb₂ particles and generates reduced grain boundaries upon the formation of nanocomposites similar to the other reports for many other systems. Obviously, the graphene in Mg₃Sb₂ matrix prevents the growth of grain boundary. The SEM-EDAX analysis (Fig 7e) clearly reveals the presence of Mg₃Sb₂ with graphene. The EDAS-mapping and line scan upto large region of sample were also probed on this nanocomposite samples to find the presence of any minor impurities other than Mg, Sb and C. Evidently, no impurities other than constituents of the nanocomposite were observed, showing the purity of the nanocomposite material.

The TEM investigation of SPSed Mg₃Sb₂ sample was carried out to check the purity of sample before it can be deployed to fabricate the nanocomposite materials. Figure 8(a) presents bright field image of Mg₃Sb₂ showing a polycrystalline sample with sizes ranging from 100nm to
500nm. A corresponding selected area electron diffraction pattern (SAEDP) shows a set of Debye rings with fine sharp spots overlapping on individual rings (Fig. 8b) confirming the material to be β-Mg₃Sb₂ hexagonal crystal structure (Space group P3₁m). Several lattice scale images (Fig. 8c) were recorded revealing different orientation of Mg₃Sb₂ and excellent crystallinity of the samples was realized. EDS analysis [Fig. 8(d)] clearly reveals the elemental Mg and Sb peaks with composition very close to the nominal Mg₃Sb₂.

Figure 9(a) represents a typical bright field electron micrograph of SPSed Mg₃Sb₂/GNS nanocomposite sample with mass ratio 80:1 showing the Mg₃Sb₂ particles with sizes ranging from 2.0 nm to 50 nm which is much smaller than the sizes of bare Mg₃Sb₂. Obviously, the Mg₃Sb₂ particles are found to be anchored on the surface of graphene nano sheets. The decrease in the sizes of Mg₃Sb₂ particles in Mg₃Sb₂/GNS nanocomposites indicates that the GNS in Mg₃Sb₂ matrix suppresses the growth of the grain boundaries which is consistent with our SEM investigation. The presence of GNS can easily be discerned in Fig 9(b & c) as the lattice fringes corresponding to GNS can be clearly identified. The HRTEM shown in the inset of Fig. 9(c) clearly shows both phases with orientational relationship (002)GNS // (101)Mg₃Sb₂. Figure 9(d) displays HRTEM image showing only Mg₃Sb₂ grains, no GNS was resolved at such high magnification. This could be due to either the microscopic condition are not optimal or depth of focus for the two phases were different to be detected simultaneously. Figure 9(f) shows the schematic reaction mechanism for the formation of Mg₃Sb₂/GNS nanocomposite.

In order to understand the impact of such novel fabricated nanocomposite with graphene as nanocomposite additive on the thermoelectric performance of bare undoped and Bi doped Mg₃Sb₂, all the nanocomposites have been subjected to thermal and electronic transport measurements. The electronic and thermal transport properties of all the nanocomposites have been compared with the parent Mg₃Sb₂ material. Figure 10 displays the temperature dependence of electrical conductivity $\sigma$, of Mg₃Sb₂/GNS nanocomposite for different mass ratios.

The electrical conductivity of all the nanocomposites increased with rising temperature displaying semiconducting behavior. Moreover, regardless of the temperature, electrical conductivity increases monotonously with increasing GNS concentration and reaches its maximum value for the nanocomposite with mass ratio 40:1. The various room temperature
physical properties are shown in table 1. The Mg$_3$Sb$_2$/GNS nanocomposites exhibit an increased electrical conductivity compared to bare Mg$_3$Sb$_2$ over the entire temperature range. The electrical conductivity $\sigma$ can be expressed by a relation as

$$\sigma = ne\mu$$

Where $n$ is the carrier concentration, $e$ is the charge of an electron and $\mu$ is the carrier mobility. Thus the enhancement in the electrical conductivity for Mg$_3$Sb$_2$/GNS nanocomposites may be attributed to either increase in carrier concentration, or an increase in carrier mobility. The table clearly demonstrates the increasing $n$ and $\mu$ with increasing GNS concentration. The maximum carrier concentration and mobility was observed for the Mg$_3$Sb$_2$/GNS nanocomposite with mass ratio 40:1. For example, $n = 7.3 \times 10^{20} \text{ cm}^{-3}$ and $\mu = 144 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the nanocomposite with mass ratio 40:1, which is much higher than that of bare Mg$_3$Sb$_2$ ($n = 1.1 \times 10^{20} \text{ cm}^{-3}$ and $\mu = 11 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). A systematic increase in the mobility was noticed in all the nanocomposites. Thus such a significant increase in the electrical conductivity is attributed primarily due to significant increase in $\mu$ and moderate increase in $n$. The rationale for this is that the pristine few layered graphene reveals p-type thermoelectric properties and the graphene with its unique 2D planar structure has ultra high electron mobility (more than 20,000 cm$^2$V$^{-1}$s$^{-1}$)$^{45}$ It has been suggested that the graphene in the nanocomposite may supply large number of extra transmission channels for electrons$^{58}$ to take part in the transport which significantly improves the electrical conductivity. We speculate that same phenomenon would have taken place in the present nanocomposites. It is worth mentioning that the explanation why graphene enhances ultrahigh $\mu$ and significantly larger $\sigma$ is entirely plausible and exact physical mechanism still requires further investigation.

The temperature dependent Seebeck coefficients for bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites are shown in Fig 11(a). The Seebeck coefficient of all the nanocomposites is positive in the whole temperature range, indicating that majority of the carriers are holes which is consistent with the Hall measurement.

With the introduction of GNS, the Seebeck coefficients at room temperature decrease for all the nanocomposites and maintained such decrement throughout the whole temperature range as
compared to that of bare Mg$_3$Sb$_2$. The decrease in Seebeck coefficient at room temperature is consistent with associated increase in carrier concentration. This phenomenon of inverse relation between $\alpha$ and $\sigma$ can be explained by the equation,

$$\alpha = \pm \frac{k_B}{e} \left[ 2 + \ln \frac{2(2\pi m^* k_B T)^{3/2}}{\hbar^3 n} \right]$$

Where $m^*$ is the effective mass relating the density of states and $n$, the carrier concentration. As noted above, the introduction of GNS induces large carrier concentration and hence according to the equation, the $\alpha$ is reduced. The absolute values of Seebeck coefficients of both bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposite increase with temperature and attain a peak values at a certain temperature, and then further followed by a decreasing trend at higher temperature. This can be accounted to an increased number of thermally excited minority carriers at higher temperature leading to decreased Seebeck coefficient. Figure 11(b) displays the power factor (PF=$\alpha^2 \sigma$) of bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites. The nanocomposites exhibit higher power factor compared to bare Mg$_3$Sb$_2$ which is mainly ascribed to the increased $\sigma$ due to introduction of GNS in the Mg$_3$Sb$_2$ matrix. The highest power factor was optimized for the Mg$_3$Sb$_2$/GNS nanocomposites with mass ratio of 80:1 at 673 K. The maximum power factor for this nanocomposite was realized to be $4.5 \times 10^{-4}$ W/mK$^2$ at 673K which is 130% larger than the bare Mg$_3$Sb$_2$ (PF=$1.98 \times 10^{-4}$ W/mK$^2$). The optimized higher power factor of Mg$_3$Sb$_2$/GNS with mass ratio: 80:1 was resulted due to a large increase in the electrical conductivity (~600% larger value than bare Mg$_3$Sb$_2$). Thus incorporation of graphene in Mg$_3$Sb$_2$ thermoelectric matrix is beneficial by increasing the electrical conductivity while inducing less effect on the Seebeck coefficient which in turn increases the large power factor (PF=$\alpha^2 \sigma$).

In addition to $\alpha$ and $\sigma$, the thermal conductivity, $\kappa$ is also an important parameter for thermoelectric material. Figure 12(a) displays the temperature dependence of thermal conductivity $\kappa$ (T) of bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites. The incorporation of GNS into Mg$_3$Sb$_2$ leads to increased thermal conductivity and increases with increasing GNS content. For instance, the total thermal conductivity ( $\kappa= 2.4$ W/mK) of Mg$_3$Sb$_2$/GNS nanocomposite for higher GNS concentration, say for 40:1 is much larger than that of Mg$_3$Sb$_2$ ($\kappa= 1.39$ W/mK).
This could be attributed to significant contribution from electronic part which could have been induced by GNS inclusions. The temperature dependent thermal conductivity of bare Mg$_3$Sb$_2$ and all the nanocomposites Mg$_3$Sb$_2$/GNS decrease with temperature, which indicates that the phonon conductivity dominates. Interestingly, the nanocomposite Mg$_3$Sb$_2$/GNS with mass ratio 80:1 displayed a low thermal conductivity at high temperature than the bare Mg$_3$Sb$_2$ which is reduced by 15% of the value of bare Mg$_3$Sb$_2$ at high temperature. The lattice thermal conductivity [Fig. 12 (c)] including bipolar was obtained by subtracting the electronic thermal conductivity from the total measured thermal conductivity. The Wiedemann-Franz law has been used to calculate the electronic thermal conductivity ($\kappa_e = L\sigma T$, where L is Lorenz number, $\sigma$, the electrical conductivity and T, the temperature in K). Here, we use the temperature dependent Lorenz number$^{91}$ and the bipolar contribution was taken into account by assuming $\kappa_{lattice} \sim 1/T^{92}$ Figure 12(c) represents the temperature dependent lattice thermal conductivity. The lattice thermal conductivity of all the samples was observed to decrease with increasing temperature (Fig. 12c), showing similar falling trend in the total thermal conductivity. The lattice thermal conductivity ($\kappa_L = 0.34$ W/mK) of Mg$_3$Sb$_2$/GNS nanocomposite at 773K is much smaller than the thermal conductivity ($\kappa_L = 0.54$ W/mK) of Mg$_3$Sb$_2$ at 773K. However, a higher $\kappa_{lattice}$ for all the nanocomposites than their respective counterparts were noted at low temperature, which might be resulted due to large lattice thermal conductivity of graphene. The rationale behind this observation could be understood by considering the properties of graphene.

The graphene has large specific surface area apart from large $\kappa_{lattice}$ and hence, an inverse effect of graphene on the thermal conductivity may also be expected. However, we anticipate that large lattice thermal conductivity is observed due to later i.e. due to high lattice thermal conductivity of graphene. The large surface area of graphene providing more interfaces to scatter phonons may not be sufficient to dominate over the large lattice thermal conductivity due to graphene addition, which needs to be further investigated. The electronic thermal conductivities, $\kappa_e$ for Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites are displayed in Fig. 12(b). Obvious increases in the $\kappa_e$ with GNS concentration for the nanocomposites were noted, owing to the increased electrical conductivities observed for the nanocomposites.
The temperature dependence of ZT of all the samples is calculated which is displayed in Fig 13(a). The ZT of the nanocomposites increases with rising temperature as presented in Fig 13(a). The maximum ZT ≈ 0.71 at temperature of 773 K for Mg$_3$Sb$_2$/GNS nanocomposite was optimized for the mass ratio 80:1, which is significantly enhanced than ZT ≈ 0.26 at 773 K for bare Mg$_3$Sb$_2$. Thus combining a large increase (~130%) in the power factor due to significant enhancement of electrical conductivity (~600%), along with 15% reduction in the thermal conductivity at high temperature, the ZT of the nanocomposite with mass ratio 80:1 was calculated to be about 170% larger than that of bare Mg$_3$Sb$_2$ sample.

Following similar strategy, GNS were also incorporated in a derivative of Mg$_3$Sb$_2$ with a nominal composition Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ to fabricate a nanocomposite of Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS and thermoelectric properties were investigated. The optimized amount of GNS in the mass ratio of 80:1 was added. The temperature dependent behavior of all the thermoelectric parameters followed consistently the similar trends. Interestingly, graphene incorporation in this case too, leads to 650% improvement in the electrical conductivity, 90% improvement in the power factor and 13% reduction in the thermal conductivity leading to a significant enhancement of ZT about 125% in comparison to that of Mg$_3$Sb$_{1.8}$Bi$_{0.2}$. Thus, graphene incorporation with its high mobility in the present Zintl phase compound provides an emerging strategy to enhance the thermoelectric performance of Mg$_3$Sb$_2$- based material. This strategy employed is summarized in fig. 13(b) which clearly presents that large $\mu/\kappa_L$ value results higher ZT and this strategy of increasing mobility by incorporating GNS in Mg$_3$Sb$_2$-based Zintl compound was successfully demonstrated at room temperature. For this strategy to be effectively seen at higher temperature, high temperature Hall measurement is required which will be future avenue of the research. We believe that this strategy is not limited to only Mg$_3$Sb$_2$ based Zintl phase compound but may be efficiently deployed for improving thermoelectric performance of other Zintl phase compounds which are largely victim with the low electrical conductivity.

Conclusion and Future Prospects:

Novel (Mg$_3$Sb$_2$,Mg$_3$Sb$_{1.8}$Bi$_{0.2}$)/GNS nanocomposites have been fabricated by incorporating graphene nanosheets in pre-synthesized Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ precursors using wet mechanical milling and further rapid heating spark plasma sintering process. The
addition of small fraction of GNS into Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ matrix resulted into the significant enhancement in the electrical conductivity (~600% and ~650% respectively) and thereby increasing to a large power factor (~130% and ~90% respectively) of thermoelectric nanocomposites material. The thermal conductivity of the nanocomposites Mg$_3$Sb$_2$/GNS and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS at higher temperature are also decreased as compared to Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$. Thus these nanocomposites outperform bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ and attain a ZT ~ 0.71 and a ZT ~ 1.35 at 773K respectively which are much larger than Mg$_3$Sb$_2$ (ZT ~ 0.26) and Mg$_3$Sb$_{1.8}$Bi$_{0.2}$ (ZT ~ 0.6) materials. Since these materials are made from abundant and non-toxic Mg, Sb and graphene and thus make them a cheap alternative and finds widespread use over high scarcity and price of Te, Pb used in commercialized state-of-the-art thermoelectric materials. A large boost in the electrical conductivity and reduced thermal conductivity at high temperature in Mg$_3$Sb$_2$/GNS nanocomposite with mass ratio 80:1 suggests that there is plenty of rooms for improvement of thermoelectric properties if a suitable concentration of GNS inclusion is optimized. It may be anticipated that an optimal amount of GNS can further refined the size of Mg$_3$Sb$_2$ particles and hence lattice thermal conductivity can be reduced for further boost in ZT of such nanocomposites. Thus design of such nanocomposites combining Zintl phase with intrinsic properties of PGEC for the potential thermoelectric materials with GNS appears to be a very effective and promising path to be followed up for improving the thermoelectric properties. Of course, this strategy is not unique to Mg$_3$Sb$_2$-based Zintl phase and may be extended to other Zintl phase compounds possessing low electrical conductivity.

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References:


68. B. Feng, J. Xie, G. Cao, T. Zhu and X. B. Zhao, *J. Mater. Chem. A*, **2013**, *1*, 13111-13119


74. E. S. Toberer, A. Zevalkink, G. J. Snyder, J. Mater. Chem. 2011, 21, 15843.
**Figure Caption:**

**Figure 1.** (a) X-ray diffraction (XRD) pattern of Mg$_3$Sb$_2$/GNS nanocomposites with mass ratio of 100:1, 80:1, 60:1, 40:1 and for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS with 80:1. Inset of fig 1(a) shows the Schematic diagram of layered crystal structure of Mg$_3$Sb$_2$ showing the anionic framework of [Mg$_2$Sb$_2$]$^{2-}$ with double layer and Mg$^{2+}$ cations between the layers. (b) Shows the TEM image of reduced GNS. Inset (fig 1b) shows the XRD of the reduced GNS. (c) HRTEM image of GNS indicating excellent crystallinity.

**Figure 2:** Shows the Raman spectra of graphene nanosheets (black color spectra) and Mg$_3$Sb$_2$/GNS nanocomposites for mass ratio 80:1(green color spectra). Inset shows the spectra for Mg$_3$Sb$_2$.

**Figure 3:** XPS survey spectrum of pure GNS, bare Mg$_3$Sb$_2$ and Mg$_3$Sb$_2$/GNS nanocomposites over wide binding energy range. All the features in the spectra have been identified. All the spectra have been staggered vertically for clarity of presentation.

**Figure 4:** C 1s core level spectra for GNS (bottom) and Mg$_3$Sb$_2$/GNS (80:1) (top). Experimental data (open circles), fitted spectra (thick solid line) and deconvoluted fitting components (shaded region) are also shown.

**Figure 5:** Mg 1s (left panel) and Sb 3d (right panel) core level spectra for bare Mg$_3$Sb$_2$ and nanocomposite Mg$_3$Sb$_2$/GNS (80:1). All the spectra have been normalized to peak height for comparison and were staggered vertically for clarity of presentation. Dashed line tracks the binding energy position.

**Figure 6:** XPS valence band spectra for bare Mg$_3$Sb$_2$ and nanocomposite Mg$_3$Sb$_2$/GNS (80:1). Inset shows the near Fermi level ($E_F$) region. Straight lines (thick solid lines) show fitting of leading edge and background. Vertical dashed lines show the position of valence band maxima (VBM). Shaded area (patterned) represents density of states between VBM and $E_F$.

**Figure 7:** (a) The SEM image of Mg$_3$Sb$_2$ showing homogeneous polycrystalline grains. (b) Energy dispersive X-ray spectrum (EDAX) of Mg$_3$Sb$_2$ indicating (inset fig. 7b) the presence of Mg and Sb and quantification results to the composition of Mg$_3$Sb$_2$ phase. (c & d) Magnified FE-
SEM image of Mg$_3$Sb$_2$/GNS nanocomposite with mass ratio 80:1 showing uniformly anchored Mg$_3$Sb$_2$ particles on the graphene nanosheets. (e) The SEM-EDAX analysis of Mg$_3$Sb$_2$/GNS nanocomposite with mass ratio 80:1 showing presence of Mg$_3$Sb$_2$ with graphene.

**Figure 8.** a) TEM image obtained from the specimen of Mg$_3$Sb$_2$ showing highly densified grains. b) SAED pattern corresponding to Mg$_3$Sb$_2$, revealing β-Mg$_3$Sb$_2$-type hexagonal structure. c) The HRTEM image of Mg$_3$Sb$_2$ exhibiting the presence of different orientations of the crystallographic planes and their interface boundaries. d) EDAX spectrum recorded from Mg$_3$Sb$_2$ confirming the composition of Mg$_3$Sb$_2$.

**Figure 9:** a) TEM image of Mg$_3$Sb$_2$/GNS (80:1) nanocomposite showing uniformly anchoring of Mg$_3$Sb$_2$ particles on the surface of graphene nanosheets. (b-c) Magnified TEM images of Mg$_3$Sb$_2$/GNS (80:1) nanocomposite showing more clearly the anchored Mg$_3$Sb$_2$ particles on to the sheet of graphene nanosheets and the inset (fig. 9c) show an orientational relationship (002)GNS//(101)Mg$_3$Sb$_2$ between the two phase. (d) HRTEM images of Mg$_3$Sb$_2$/GNS (80:1) nanocomposite showing only Mg$_3$Sb$_2$ grains, no GNS was resolved at such high magnification. (f) Schematic diagram of reaction mechanism occurred during the fabrication of Mg$_3$Sb$_2$/GNS nanocomposite.

**Figure 10:** Temperature dependence of Electrical conductivity of Mg$_3$Sb$_2$/GNS nanocomposite with mass ratio 100:1, 80:1, 60:1, 40:1 and for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS nanocomposites with mass ratio 80:1.

**Figure 11:** Temperature dependence of (a) Seebeck coefficient and (b) power factor of Mg$_3$Sb$_2$/GNS nanocomposites with mass ratio of 100:1, 80:1, 60:1, 40:1 and for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS nanocomposite with mass ratio 80:1.

**Figure 12:** Temperature dependence of (a) Thermal conductivity ($\kappa$), (b) Electronic thermal conductivity ($\kappa_e$) and (C) lattice thermal conductivity ($\kappa_L$) of Mg$_3$Sb$_2$/GNS nanocomposites with mass ratio of 100:1, 80:1, 60:1, 40:1 and for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS with 80:1.

**Figure 13:** (a) Temperature dependence of thermoelectric figure of merit (ZT) of Mg$_3$Sb$_2$/GNS nanocomposites with mass ratio of 100:1, 80:1, 60:1, 40:1 and for Mg$_3$Sb$_{1.8}$Bi$_{0.2}$/GNS nanocomposites with mass ratio of 80:1.
260x137mm (150 x 150 DPI)
Mg 1s
- Mg₃Sb₂:GNS (80:1)
- Mg₃Sb₂

Sb 3d
- Mg₃Sb₂:GNS (80:1)
- Mg₃Sb₂
191x180mm (150 x 150 DPI)
The diagram shows the thermoelectric figure of merit (ZT) as a function of temperature (K) for different MgSb compounds and their composites with GNS. The ZT values are plotted against the ratio of electrical conductivity ($\mu$) to thermal conductivity ($k_L$). The graph highlights the improved thermoelectric performance at higher temperatures for composite materials compared to pure MgSb.
### Table 1. Showing composition and various physical parameters

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Nominal Composition</th>
<th>Actual Composition (SEM-EDAX)</th>
<th>Electrical Conductivity $\sigma$ ($10^3$ S/m)</th>
<th>Hall Coefficient $R_H$ ($10^{-2}$ cm$^2$/V/s)</th>
<th>Carrier Conc. $n$ ($10^{20}$ cm$^{-3}$)</th>
<th>Mobility $\mu$ (cm$^2$/V·s)</th>
<th>Seebeck Coefficient $\alpha$ (µV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Mg$_3$Sb$_2$</td>
<td>Mg$<em>{60.54}$Sb$</em>{39.46}$</td>
<td>0.206</td>
<td>5.02</td>
<td>1.2</td>
<td>11</td>
<td>193.2</td>
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<tr>
<td>2.</td>
<td>Mg$_3$Sb$_2$/GNS (100:1)</td>
<td>C$<em>{4.87}$Mg$</em>{56.94}$Sb$_{38.29}$</td>
<td>9.61</td>
<td>1.01</td>
<td>5.3</td>
<td>108.3</td>
<td>120.39</td>
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<tr>
<td>3.</td>
<td>Mg$_3$Sb$_2$/GNS (80:1)</td>
<td>C$<em>{6.12}$Mg$</em>{55.86}$Sb$_{38.02}$</td>
<td>12.35</td>
<td>0.98</td>
<td>6.1</td>
<td>121.7</td>
<td>111.41</td>
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<tr>
<td>4.</td>
<td>Mg$_3$Sb$_2$/GNS (60:1)</td>
<td>C$<em>{8.41}$Mg$</em>{54.68}$Sb$_{36.91}$</td>
<td>15.56</td>
<td>0.87</td>
<td>6.9</td>
<td>135.9</td>
<td>97.02</td>
</tr>
<tr>
<td>5.</td>
<td>Mg$_3$Sb$_2$/GNS (40:1)</td>
<td>C$<em>{11.38}$Mg$</em>{52.46}$Sb$_{35.13}$</td>
<td>17.49</td>
<td>0.82</td>
<td>7.3</td>
<td>144</td>
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<td>6.</td>
<td>Mg$<em>3$Sb$</em>{1.8}$Bi$_{0.2}$</td>
<td>Mg$<em>{59.92}$Sb$</em>{36.45}$Bi$_{1.03}$</td>
<td>0.358</td>
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<td>1.4</td>
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<td>305.43</td>
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<td>7.</td>
<td>Mg$<em>3$Sb$</em>{1.8}$Bi$_{0.2}$/GNS (80:1)</td>
<td>C$<em>{7.12}$Mg$</em>{64.51}$Sb$<em>{33.26}$Bi$</em>{5.11}$</td>
<td>13.35</td>
<td>0.95</td>
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<td>139.78</td>
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