Improved trade-off between thermoelectric performance and mechanical reliability of Mg$_2$Si by hybridization of few-layered reduced graphene oxides

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Siilicide-based thermoelectric (TE) compounds have received much attention as potential candidates for automotive TE generators (ATEGs) owing to their low density, environmental friendliness, and competitive price. In particular, n-type Mg$_2$Si is the most suitable for ATEGs because it has very low density (~1.59 g/cm$^3$) and low material cost (~$91/kg) compared to other candidates (filled skutterudite: density ~7.8 g/cm$^3$ and cost ~$562/kg; half-Heusler: density ~8.5 g/cm$^3$ and cost ~$151/kg) [1,2]. Owing to these advantages, research has focused on enhancing the TE conversion efficiency (TE figure of merit, $ZT = \sigma^2S^2/T/\kappa_t$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the absolute temperature, and $\kappa_t$ is the total thermal conductivity) of Mg$_2$Si-based compounds, and the maximum $ZT$ value attained was 1.2 @ 700 K [2], which is comparable to those of other commercial TE compounds (filled skutterudite Ba$_{9.86}$Al$_{0.02}$Si$_{10.97}$B$_{0.03}$: $ZT = 1.7 @ 835 K$, half-Heusler Hf$_{0.67}$Zr$_{0.22}$Ni$_{0.08}$Sn$_{0.99}$Sb$_{0.01}$: $ZT = 1.0 @ 873 K$) [3,4]. These high $ZT$ values of TE materials enable the generation of sufficient power for mid-to-high-temperature applications, and facilitate research on modularization and system development. A key prerequisite is to secure the lifetime of a TE system for commercialization, which is directly related with the mechanical, chemical, and thermal reliability of the TE materials at higher temperatures. Mechanical reliability is the most important parameter in the use of ATEGs owing to vibrational conditions; however, Mg$_2$Si-based compounds have a lower mechanical reliability ($K_c = 0.82$ MPa m$^{1/2}$) compared to other TE materials. The fracture toughness ($K_c$) of higher manganese silicide is ~1.03 MPa m$^{1/2}$, whereas those of filled skutterudite and half-Heusler are ~1.5 MPa m$^{1/2}$ and ~2.2 MPa m$^{1/2}$, respectively [5–8].

Nanocomposite (introduction of nanophases in the TE matrix) would be an effective approach to enhance the mechanical properties of the TE matrix. It also improves the electronic and/or thermal transport properties in many TE compounds. Well-designed nanophases, when introduced in a monodispersed form, are expected to improve the power factor ($\sigma^2S^2$) owing to the carrier-filtering effect or modification of the electronic structure [2,9]. Moreover, it is possible to reduce the lattice thermal conductivity ($\kappa_{lat} = \kappa_{tot} - \kappa_{ph}$, where $\kappa_{ph}$ is the electronic contribution of thermal conduction) by promoting phonon scattering even at a relatively low volume fraction of nanophases [10,11]. However, several vol.% of nanophases need to be introduced to improve the mechanical reliability, considering crack propagation [12]. Control of the characteristics of the nanophases (dimension, size, type, morphology, and intrinsic properties) will be crucial for the simultaneous improvement of TE and mechanical properties, especially in Mg$_2$Si-based compounds, since the mean free paths for electrons and phonons

A B S T R A C T
Nanocomposites can simultaneously enhance the thermoelectric and mechanical properties of thermoelectric materials. Here, we fabricated bulks of Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ with monodispersed few-layered reduced graphene oxides utilizing ultrasonic-based wet chemical pulverizing-mixing and spark plasma sintering to improve unfavorable trade-off between thermoelectric performance and mechanical reliability, which is important for commercialization. An unexpected high fracture toughness of ~1.88 MPa m$^{1/2}$ was observed due to the synergistic effect of the deflection of crack propagation, bridging, and sheet pull-out mechanisms, and a high thermoelectric figure of merit ~0.6 was obtained even for a high content (3 vol.%) of reduced graphene oxides.

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are similar (~20 nm) [13]. An enhanced power factor could be obtained only in nanocomposites with a very small amount of nanophases, while nanocomposites with several vol.% of the nanophases showed severely deteriorated electronic transport properties (Table S1), as expected by theoretical calculations for nanostructured silicide-based TE materials [14].

In this respect, low-dimensional carbon-based nanomaterials such as graphene, rGO, and carbon nanotubes (CNTs) are good candidates as they can possibly lead to increased interface density as well as outstanding mechanical and electrical properties. Recently, remarkable results were reported for skutterudite-based nanocomposites; $\kappa_c$ and $ZT$ values of filled skutterudites were simultaneously enhanced by the introduction of several vol.% of rGO and CNT [12,15,16].

In a previous study, we determined $ZT$ and $K_c$ using monodispersed Sn nanoparticles (~100 nm)-embedded Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$. Moreover, the interface density was found to be the key parameter to determine both electronic and thermal transport properties. Particularly in carbon-based nanophases such as rGO, CNT, and graphene, the dependence of TE transport properties on the dispersibility becomes more important owing to detrimental effects arising in the presence of agglomerated carbon. As shown in Table S2, well-controlled and monodispersed carbon nanophases led to enhanced TE performance in commercial TE materials. We fabricated bulk nanocomposites of Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ with monodispersed few-layered rGO by SPS compaction of hybrid powders of Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ and rGO. Notably, hybrid powders of Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ (~3 μm) with monodispersed few-layered rGO were obtained (Fig. 1(c)). The size of the rGO in the hybrid powders was maintained at the level of as-prepared rGO, owing to its high mechanical strength. Interestingly, Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ powders wrapped by rGO were observed in the hybrid powders (Fig. 1(c)).

The microstructure of the SPS-compactd bulk nanocomposites was confirmed by SEM analysis of the fractured surface. As shown in Fig. S5, grain growth during SPS was not significant; the average grain size of the bulk nanocomposites was ~3 μm, similar to that of the powder, suggesting that rGO acts as a grain growth inhibitor. Owing to the reduced grain size of the nanocomposites, the relative densities (~93%) decreased and the fraction of MgO increased compared to the pristine sample (Fig. S6) [20]. The detailed positions and morphology of the rGO in the bulk nanocomposites were obtained by TEM. TEM/EDS analysis revealed that few-layered rGO with an average thickness of ~5 nm was located at the grain boundaries (Fig. 1(d), (e)). rGO-wrapped Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ found in the hybrid powders was also observed in the bulk, and was similar in morphology to the nanocomposite of Ce$_3$Fe$_2$Co$_2$Si$_2$ and rGO [15].

The temperature dependence of $\sigma$ and $S$ of the nanocomposites as a function of rGO contents was determined to investigate the effect of rGO at the grain boundaries on the electronic transport properties (Fig. 2). rGO at the grain boundaries might contribute to improving the electronic transport properties of TE materials. For example, enhanced $\sigma$ has been reported in ZnO systems due to the modification of the band structure for rGO and Al-doped ZnO; a higher $\mu_{\text{Hall}}$ corresponding to those of single crystals was realized [21]. However, the $\sigma$ values of the nanocomposites were lower than those of the pristine sample, and decreased with rGO content throughout the measured temperature range, suggesting that electron carriers would be scattered by rGO. To clarify this, we calculated $n_s$ and $\mu_{\text{Hall}}$ by considering a one-band model, and have represented them in Fig. S7(a). The reduction in $\sigma$ was related with the decrease in $n_s$ (9.27 × 10$^{19}$ cm$^{-3}$ for the pristine sample, 8.82 × 10$^{19}$ cm$^{-3}$ for 1 vol.% rGO nanocomposite, and 1.92 × 10$^{19}$ cm$^{-3}$ for 4 vol.% rGO nanocomposite) due to carrier recombination, and $\mu_{\text{Hall}}$ (81.4 cm$^2$ V$^{-1}$ s$^{-1}$ for the pristine sample, 57.9 cm$^2$ V$^{-1}$ s$^{-1}$ for 1 vol.% rGO nanocomposite, and 23.6 cm$^2$ V$^{-1}$ s$^{-1}$ for 4 vol.% rGO nanocomposite) due to scattering at the interfaces between rGO and Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$. Additionally, a sharp decrease in $S$ at lower temperatures occurred by the formation of MgO.

The absolute values of $S$ slightly increased with the rGO content mainly due to the reduced $n_s$. However, the calculated power factor values of the bulk nanocomposites (2.39–0.62 mW m$^{-1}$ K$^{-2}$ for 1–4 vol.% rGO nanocomposites) were much lower than that of the pristine sample (2.72 mW m$^{-1}$ K$^{-2}$). The decrease in $\mu_{\text{Hall}}$ is one reason. Another important reason for this is the unfavorable trade-off relationship between $\sigma$ and $S$ in Mg$_{1.96}$Si-based compounds [13,20]. Other commercial TE materials including filled skutterudite- and Bi-Te-based alloys show the general $\sigma$ and $S$ trade-off found in most TE semiconductors, yielding high power factor values in a wide $n_s$ range. However, high power factor values can be obtained within a very narrow $n_s$ window in Mg$_{1.96}$Si-based compounds, indicating that the $n_s$ of the matrix should be tuned to the level of the maximum power factor by considering $n_s$ variation from the nano-phases.

The temperature dependence of the $\kappa_{\text{tot}}$ values of the nanocomposites as a function of rGO contents (Fig. 3(a)) was determined to investigate the effect of rGO at the grain boundaries on the thermal transport properties. The $\kappa_{\text{tot}}$ values of the bulk nanocomposites (3.74–4.75 W m$^{-1}$ K$^{-1}$ at 373 K and 2.06–2.70 W m$^{-1}$ K$^{-1}$ at 873 K)
were found to be lower than that of the pristine sample (5.06 W m\(^{-1}\) K\(^{-1}\) at 373 K and 2.89 W m\(^{-1}\) K\(^{-1}\) at 873 K); as the rGO content increases, \(\kappa_{\text{tot}}\) tends to decrease gradually. To ascertain the scattering mechanism, we calculated \(\kappa_{\text{lat}}\) by subtracting the electronic contribution \(\kappa_{\text{ele}}\) from \(\kappa_{\text{tot}}\). The Lorenz number (\(L\)) was calculated as shown in the supplementary material. The bulk nanocomposites have lower \(\kappa_{\text{lat}}\) values compared to that of the pristine sample (Fig. 3(b)) owing to intensified phonon scattering in the presence of rGO, while a higher rGO content resulted in a rather increased \(\kappa_{\text{lat}}\) due to the contribution of rGO with a very high \(\kappa\) of ~3000 W m\(^{-1}\) K\(^{-1}\) based on the rule of mixtures (Fig. S7(b)). The estimated \(ZT\) values of the nanocomposites were lower (0.29–0.77 at 873 K) than that of the pristine sample (0.82 at 873 K) due to the decrease in power factor. However, the decrease in \(ZT\) in the rGO-introduced nanocomposites was rather moderate compared to that for the Sn nanoparticles-embedded nanocomposites [17] with the same volume fraction of nanophases (Fig. 4(c)). Reduced \(\kappa_{\text{lat}}\) values were obtained both in the nanocomposites with two-dimensional rGO and three-dimensional Sn nanoparticles; however, phonon scattering by the nanophases was not significant, because the main phonon scattering center in Mg\(_2\)Si is the point defect [14].

These features of the electronic and thermal transport properties suggest that rGO is more favorable than metal nanoparticles for the preparation of Mg\(_2\)Si-based nanocomposites.

Fig. 1. (a) Schematic diagram of the ultrasonic-based wet pulverizing-mixing process, SEM images of the (b) pristine Mg\(_{1.96}\)Al\(_{0.04}\)Si\(_{0.97}\)Bi\(_{0.03}\) powders and (c) hybrid powders of Mg\(_{1.96}\)Al\(_{0.04}\)Si\(_{0.97}\)Bi\(_{0.03}\) and rGO with 3 vol.%, and (d, e) TEM images of the 3 vol.% rGO bulk nanocomposite. The inset in (e) shows the TEM/EDS image of the bulk nanocomposite.
measured $K_c$ at 10 different points for each sample to ensure the reliability of the measurement. The $K_c$ values of the nanocomposites (1.12–2.06 MPa m$^{1/2}$) increased with rGO contents, and were comparable to that of the p-type counterpart higher manganese silicide (~1.63 MPa m$^{1/2}$) [5]. A microhardness indentation image of the bulk nanocomposite with 3 vol.% rGO is shown in Fig. 4(a). The insets of Fig. 4(a) show three different mechanisms for $K_c$ enhancement; deflection of crack propagation, bridging of the crack, and sheet pull-out within the crack. The improved $K_c$ by the deflection of crack propagation typically occurs by the introduction of any type of nanophase. The dimension of the nanophases is not important for this mechanism; instead, increase in the density of the nanophases is important. $K_c$ enhancement by bridging the crack and sheet pull-out within the crack can only be induced by low-dimensional nanophases, since these two mechanisms arise due to the absorption of crack propagation energy. Moreover, increasing the contact area with the matrix by the introduction of two-dimensional rGO will require more energy than for a one-dimensional nanofiber [22]. Owing to the difference in $K_c$ enhancement mechanisms with the dimensionality of the nanophases, the $K_c$ values of the nanocomposites with two-dimensional rGO were much higher than those of nanocomposites with the three-dimensional Sn nanoparticles, especially at higher volume fraction [17].

From Fig. 4(c) and (d), we discovered an important trade-off relationship between the TE ($ZT$) and mechanical properties ($K_c$). We calculated $\frac{K_c}{K_{c,\text{ref}}} \times \frac{ZT}{ZT_{\text{ref}}}$, which can directly provide numerical information about this trade-off (Fig. 4(e)). Although the reduction of $ZT$ by the introduction of nanophases was unavoidable, the trade-off between $ZT$ and $K_c$ was significantly improved by the controlled introduction of the few-layered rGO. We emphasize that the trade-off between $ZT$ and mechanical reliability should be investigated before module and system fabrication. Our results could aid in establishing design guidelines for the development of bulk TE nanocomposites for power generation applications.

We developed Mg$_2$Si-based thermoelectric nanocomposites with enhanced fracture toughness (~1.88 MPa m$^{1/2}$) and a high $ZT$ of 0.6 at 873 K by the introduction of 3 vol.% few-layered rGO (~5 nm in thickness). The high density of interfaces between the Mg$_{1.96}$Al$_{0.04}$Si$_{0.97}$Bi$_{0.03}$ matrix and two-dimensional rGO leads to significantly improved fracture toughness. Owing to the intrinsic characteristics of the electronic and thermal transport of Mg$_2$Si, deterioration of electronic transport
properties could not be completely prevented in the presence of nanophases; however, we could significantly reduce carrier scattering by the well-controlled introduction of rGO. We also found that the carrier concentration of the Mg2Si matrix should be tuned by considering the variation from the nanophases to obtain a high power factor in nanocomposites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scriptamat.2018.11.052.

References
