Maximizing the performance of n-type Mg$_3$Bi$_2$ based materials for room-temperature power generation and thermoelectric cooling

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Although the thermoelectric effect was discovered around 200 years ago, the main application in practice is thermoelectric cooling using the traditional Bi$_2$Te$_3$. The related studies of new and efficient room-temperature thermoelectric materials and modules have, however, not come to fruition yet. In this work, the electronic properties of n-type Mg$_{3.2}$Bi$_{1.5}$Sb$_{0.5}$ material are maximized via delicate microstructural design with the aim of eliminating the thermal grain boundary resistance, eventually leading to a high $zT$ above 1 over a broad temperature range from 323 K to 423 K. Importantly, we further demonstrated a great breakthrough in the non-Bi$_2$Te$_3$ thermoelectric module, coupled with the high-performance p-type $\alpha$-MgAgSb, for room-temperature power generation and thermoelectric cooling. A high conversion efficiency of ~2.8% at the temperature difference of 95 K and a maximum temperature difference of 56.5 K are experimentally achieved. If the interfacial contact resistance is further reduced, our non-Bi$_2$Te$_3$ module may rival the long-standing champion commercial Bi$_2$Te$_3$ system. Overall, this work represents a substantial step towards the real thermoelectric application using non-Bi$_2$Te$_3$ materials and devices.
The long-term climate policy, an economy with net-zero greenhouse gas emissions by 2050, is significantly affecting the global economic situation, which stimulates the rapid development of clean and sustainable energy-related technologies. Among them, thermoelectric effect can directly convert the temperature gradient to electricity and vice-versa. Despite the relatively low performance, thermoelectric devices have these unique advantages, including high reliability and scalability, no pollution and no noise, precise temperature control, enabling them suitable for a range of potential applications, such as aerospace power, refrigeration, and even energy harvesting. The corresponding thermoelectric conversion efficiency or the cooling coefficient of performance (COP) is mainly determined by the dimensionless thermoelectric figure of merit ($zT$), which is defined as $zT = [S^2σ/(k_f + κ_{dev})]T$, where $S$, $σ$, $κ_{dev}$ and $T$ are Seebeck coefficient, electrical conductivity, lattice thermal conductivity, electronic thermal conductivity, and absolute temperature, respectively.

In general, the material's thermoelectric performance is dominated by its crystal structure, specific composition, as well as nano-microstructure. Despite the intertwined relationship, the rational compromise and synergy among these abovementioned factors enable the realization of a maximum $zT$ for a given material. Previous investigations mainly focused on the modification of electronic band structure by elements alloying and/or tuning the phonon-scattering mechanism by designing special microstructure. Very recently, the significance of grain-boundary resistance on the low-temperature charge transport has been recognized in some material systems. This frequently overlooked effect leads to a lower charge carrier mobility and deteriorated practical $zT$s compared to their predicted values.

Bi$_2$Te$_3$ related alloys, which are discovered around the 1950 s as the best room-temperature thermoelectric material, are used in the commercial cooling area. However, one of the main reasons that limit its further wide applications is the scarcity of Tellurium (Te) element. During the past decade, some new Te-free thermoelectric candidates with high $zT$s, such as α-MgAgSb$_2$, Mg$_3$P$_2$, SnTe$_3$, enable the potential replacement of Bi$_2$Te$_3$, in which a high power-generation performance of Mg$_2$Sb$_2$/MgAgSb module, with the target for harvesting low-temperature waste heat, has already been demonstrated very recently. P-type α-MgAgSb shows the large enhancement of thermoelectric performance at the low-temperature range by suitable doping. Alloying with Mg$_2$Bi$_2$ in n-type Mg$_2$Sb$_2$ yields the optimum bandgap and simultaneously strengthens the point-defect scattering, therefore contributing to highly competitive $zT$s. Moreover, a high-performance uni-couple (with p-type Bi$_2$Sb$_2$Te$_3$ for thermoelectric cooling has been experimentally realized. However, there is still no report about non-Bi$_2$Te$_3$ Peltier module thus far, due to a combination of the complicated synthesis method and the challenging module-fabrication process for these non-Bi$_2$Te$_3$ thermoelectric systems. Very recently, thermoelectric module consisting of n-type Bi$_2$Te$_3$ and p-type SnSe showed a maximum temperature difference $ΔT_{max}$ of 45.7 K, being attractive for future applications.

Herein, the thermoelectric performance of Mg$_2$(Bi, Sb)$_2$ system was fully maximized through rational microstructural design to eliminate the intrinsic grain-boundary resistance, which contributed to a higher $z’$ than the commercial n-type Bi$_2$Te$_3$ above room temperature (Fig. 1a). Coupled with the optimized p-type α-MgAgSb (Fig. 1a), we demonstrated a remarkably high thermoelectric performance of non-Bi$_2$Te$_3$ and 8-pairs module for room-temperature power generation and thermoelectric cooling. These images of both the fabricated module and the cooling-performance measurement setup were given here (Fig. 1b). Specifically, at the $ΔT$ of 35 K, the $η$ and the maximum output power $P_{max}$ reached 0.95% and 0.016 W (Fig. 1c), respectively. Moreover, the peak $η$ reached 2.8% associated with a $P_{max}$ of 0.12 W at the $ΔT$ of 95 K. The calculated output power density of our fabricated module, with a whole cross-sectional dimension of $18 \times 15$ mm, was comparable to the zone-melting Bi$_2$Te$_3$ module (Fig. S1). Meanwhile, for cooling applications, when working at the optimum electric current $I$ with a hot-side temperature $T_h$ of 323 K, the $ΔT_{max}$ and the maximum cooling power $P_{max}$ could reach 56.5 K and 3.0 W (Fig. 1d), respectively. The achieved thermoelectric performance of our fabricated module is higher than the recently reported high-performance SnSe/Bi$_2$Te$_3$ module, even comparable to the commercial Bi$_2$Te$_3$ module (Fig. 1e). Considering the billion-US-dollar market for the global thermoelectric Peltier module, this work brings promise for non-Bi$_2$Te$_3$ thermoelectric cooling and therefore paves up the avenue for emerging cooling technology.

**Results and discussion**

To possess the optimum bandgap for the room-temperature application, it is imperative to shift the target material of Mg$_3$(Bi, Sb)$_2$ system from Sb-rich to Bi-rich. Hence, Mg$_2$Bi$_2$Sb$_3$ is chosen as the basic composition, and doping with a little Te enables to tune the carrier concentration. Since minor Cu addition in Mg$_2$Sb$_3$Bi$_3$ realized the remarkable enhancement of low-temperature $zT$, herein the nominal composition is Mg$_2$Bi$_2$Sb$_3$. We revealed that the spark plasma sintering (SPS) temperature has a noticeable impact on the thermoelectric properties, which is beyond the conventional understanding that sintering temperature only affects the densification mechanism or main-phase change. The phase feature when sintered at the different temperatures was thoroughly investigated by a combination of X-ray diffraction (XRD) analysis, in situ SPS displacement record, and differential scanning calorimetry (DSC) measurement. Apparently, no impurity phase can be observed for the sample sintered at 723 K (Fig. 2a). In contrast, Bi impurity phase starts to appear at a higher sintering temperature than 723 K (Fig. S2). Meanwhile, the significant evaporation and the appearance of the squeezed melting phase are observed simultaneously (Fig. S3). Furthermore, XRD pattern of the melting-phase reveals that it consists of two different phases (Fig. 2b), namely Bi and Mg$_2$(Bi, Sb)$_2$. This should be related to the high-temperature decomposition of Mg$_2$(Bi, Sb)$_2$ due to its intrinsic instability, which is revealed through synchrotron powder XRD measurements along with synchrotron X-ray total scattering during repeated thermal cycling of Mg$_2$Sb$_3$Bi$_4$Te$_9$ powder reported by Jørgensen et al. This phenomenon can be further confirmed by the in situ recorded SPS displacement during the sintering process (Fig. 2c). For the sample sintered at 1073 K, there exist three independent plateaus that are distinct from other samples: the first one appears at the sintering-temperature range of 623–773 K, the second one during 843–1000 K, as well as the third one at the 1073 K iso-thermal process. These two melting phases are squeezed out during these abovementioned temperature ranges meanwhile Mg evaporation leads to the formation of nano-micro pores. As the utilization rate of raw materials is not 100%, the squeezed melting phase is associated with a little economic loss. For the heating DSC measurement (Fig. 2d), the exothermic peak at 858 K may be due to relaxing the lattice strain since the previous report claimed the origin of the crystalline Bi phase is caused by a reduction of microscopic strain in the structure, while the subsequent endothermic reaction should be related to the severe partial decomposition reaction.

In addition to the phase component, tuning the sintering-temperature affects the microstructural feature considerably. As
revealed by Scanning Electron Microscopy (SEM) analysis, the grain size has remarkably increased from several hundred nanometers (sintered at 723 K) to dozens of micrometers (sintered at 1073 K). In addition, the grain morphology has changed from the equiaxed structure (at 723, 873, and 973 K) to the columnar structure (at 1073 K) (Fig. 3), in which the columnar-structure characteristic can be observed in the corresponding low-magnification SEM image (Fig. S4). This is due to the liquid compact sintering effect at the high-temperature that is favorable to the formation of the large and anisotropic grain, as revealed in the previous report51. Simultaneously, sintering at 1073 K leads to the larger pores size and higher porosity as a direct consequence of Mg evaporation, whereas sintering at 723 K is unable to realize the dense compact, which can be reflected by the measured sample density (Table S1). Since Mg has a higher saturated vapor pressure than Sb and Bi at a defined temperature, the real chemical composition measured by SEM + EDS proved the Mg loss for sintering at high temperatures (Table S2), consistent with the annealing result of Mg3(Bi, Sb)252. Clearly, the pores inside the sample start to appear when the sintering temperature is above 873 K (Fig. S5). In addition, the number of pores, namely the amount of evaporation, is gradually increased with the sintering temperature. However, it is difficult to observe the SPS displacement caused by the Mg evaporation during the sintering
process since the impact of Mg evaporation is less significant compared to the melting-phase sequent out process.

The microstructural evolution originated from tuning the sintering-temperature effect was illustrated schematically (Fig. 4a). Briefly, sintering at the appropriate temperature realizes the large grain size with small pores and simultaneously minor Cu addition beneficially modifies the grain-boundary complexions with high electrical conductivity, both of which contribute to the observed high charge carrier mobility $\mu_H$. A high $\mu_H$ around 290 cm$^2$ V$^{-1}$ s$^{-1}$ can be realized in our work through rationally designing the microstructure (Fig. 4b), which is much higher than these reported Mg$_3$Bi$_2$ based samples at the same carrier concentration $n_H$ from Mao et al. and Imasato et al. It should be noted that at the too-high sintering temperature (at 1073 K), due to both the large pore size and the high porosity, $\mu_H$ deteriorates remarkably in turn that was about 22 times less compared to the maximum value. The weighted mobility $\mu_W$ is a good tool to assess the potential of the material's electronic properties in thermoelectric, which is independent of the doping element and/or real $n_H$. Generally, $\mu_W$ is codetermined by the drift mobility $\mu_D$ and the density of states effective mass $m^*$, shown in the following equation:

$$\mu_w = \frac{\mu_D m^*}{m_e}$$

where $m_e$ is the electron mass. The calculation method was according to the simplified mathematic model proposed by Zhu et al. (Table S3). Due to the high $\mu_H$, the sample (sintering at 973 K) possesses the highest $\mu_W$ in the Mg$_3$(Bi, Sb)$_2$ system that shares the same tendency with $\mu_H$ (Fig. 4c), indicative of the good electronic quality of our synthesized samples.

Tuning the sintering temperature eliminates the thermal grain-boundary resistance and therefore observably reduces the electrical resistivity $\rho$ at the low-temperature range (Fig. 5a). In comparison to these optimized samples from Mao et al. and Imasato et al. our synthesized sample (~973 K) shows the lowest $\rho$ at the whole measured temperature range, due to the combined advantage from tuning the sintering temperature and minor Cu addition. However, the tendency of $n_H$ as a function of sintering temperature is not regular, probably caused by the real-composition change and/or the severe decomposition process at...
**Fig. 4** The effect of tuning the sintering temperature on the electronic properties of Mg$_{3.2}$Bi$_{1.5}$Sb$_{0.498}$Te$_{0.002}$Cu$_{0.01}$ samples. (a) The schematic diagram of microstructural evolution when tuning the sintering temperature, (b, c) the measured charge carrier mobility $\mu_H$ values and the predicted weighted mobility $\mu_W$ as a function of carrier concentration $n_H$, respectively, in comparison with the data from Mao et al. and Imasato et al.$^{25,26}$.

**Fig. 5** Temperature-dependent thermoelectric properties of Mg$_{3.2}$Bi$_{1.5}$Sb$_{0.498}$Te$_{0.002}$Cu$_{0.01}$ samples at different sintering temperatures (723, 873, 973, and 1073 K), in comparison to the data from Mao et al. and Imasato et al.$^{25,26}$. (a–d) Electrical resistivity $\rho$, Seebeck coefficient $S$, total thermal conductivity $\kappa_{tot}$, and thermoelectric figure of merit $zT$, respectively.
1073 K. Seebeck coefficient $S$, however, shows the anomalous tendency (Fig. 5b), irrespective of the $\rho$ or $n_T$. This is in good agreement with these previous reports in Mg$_3$Sb$_1$.5Bi$_{0.55}$,55,56. As a result of the reduced $\rho$, power factor $PF$ shows a significant enhancement by optimizing the sintering temperature, in which the highest $PF$ in our work surpasses 30 $\mu$W cm$^{-1}$ K$^{-2}$ (Fig. S6). Here it should be noted that the obtained $S$ measurement results show some discrepancy between the commercial ZEM-3 and the homemade apparatus in the work of Imasato et al.26 probably due to the cold-finger effect, which may underestimate somewhat the measured $PF$ from Imasato et al.26. Combined with the thermal conductivity $\kappa_{\text{hot}}$ (Fig. 5c), tuning the sintering temperature significantly enhances the thermoelectric figure of merit $zT$, in which $zT$ above 1 over a broad temperature range from 323 to 423 K is achieved accompanied with a high room-temperature $zT$ close to 0.9 that is the record-high value in the Mg$_3$Sb$_2$ system (Fig. 5d).

To further evaluate the potential of our synthesized material for the room-temperature thermoelectric application, an 8-pairs thermoelectric module, consisting of n-type Mg$_{3.2}$Bi$_{2.1}$Sb$_{0.9}$Te$_{0.9}$ (sintered at 973 K) and p-type Mg$_{3.2}$Bi$_{2.1}$Sb$_{0.9}$ (sintered at 973 K), was designed and successfully fabricated. MgAgSb, as a high-performance and mechanically robust thermoelectric material, is a promising substitute candidate for p-type (Bi, Sb)$_2$Te$_3$.24 Cu doping can further optimize thermoelectric properties, leading to a higher average $zT$ (Fig. S7). Concerning the module details, the fabrication method and the corresponding measurement principle, as well as the stimulation theory of theoretical performance were given in the following methods part. First, we performed the three-dimensional finite-element simulations of both power-generation and cooling performance with COMSOL Multiphysics® software in the Heat Transfer Module to optimize the leg geometry and length, shown in Figs. S8, S9, respectively. The theoretical temperature distribution of our fabricated module is obtained at the hot-side temperature of 373 K (Fig. 6a). Under the optimized $I$ of 0.8 A, the maximum $\eta$ is 2.8% at the hot-side temperature of 373 K, namely under the temperature difference of 95 K (Fig. 6b). This achieved high $\eta$ can be comparable to the best Bi$_2$Te$_3$ module produced in a research laboratory46,57, but a little lower than the high-performance type commercial module from KELK Ltd58 (Fig. 6c). However, the difference between the measured value and theoretical stimulation (dash line in Fig. 6b) is still noticeable. This is primarily due to the larger internal resistance $R$ as a consequence of the relatively large interfacial resistance between the interfacial layer and element material for both n-type and p-type legs, leading to the lower output power $P$ and $\eta$ in comparison to the theoretical stimulation (Fig. S10). Herein, the interfacial layers of n-type and p-type leg are pure Fe and Ag layers, respectively, both of which do not show the obvious voltage jump around the interface (Fig. S11). Besides, their corresponding EDS mapping images further indicate no observable elemental diffusion (Figs. S12, S13). The interfacial resistance of the present n-type and p-type legs is around 20 $\mu$Ω cm$^{-2}$, a little higher than the threshold value of 5 $\mu$Ω cm$^{-2}$ accepted for thermoelectric modules with a short leg around 1–2 mm59. The resistivity of n-type leg is approximately consistent with that of sample without interfacial layer. However, it is twice larger in p-type leg. The SPS condition must be optimized with elements adding interfacial layer for further improvement. In contrast, the open-circuit voltage $V_{oc}$ and the maximum heat dissipated from the cold side of the module $Q_{\text{max}}$ are basically consistent with the simulation results (Fig. S14), which indicates the good accuracy of $S$ and $\kappa$ measurement, respectively. Regarding thermoelectric cooling, the theoretical cooling temperature difference of our
fabricated module is obtained at the condition of the hot-side temperature of 323 K, air temperature of 303 K, as well as the working current I of 5 A (Fig. 6d). Specifically, one of the most important indexes is the cooling coefficient of performance (COP) that represents the ratio of the amount of heat absorbed Qc to the total electrical power input P, as COP = Qc/P. The maximum COP of our fabricated module, under the temperature difference of 10 and 20 K, reaches 2.6 and 1.0 (Fig. 6e), respectively, with the hot-side temperature Tfi as 323 K. Importantly, an expected higher COP value, as well as a larger both ΔTmax and Qmax can be possibly achieved if the contact resistance can be further reduced (Figs. 6e, S15). Our achieved performance can be comparable with the commercial Bi1Te3 thermal electric module (Fig. 6f). The demonstration of remarkably high thermoelectric performance in a non-Bi2Te3 module holds great promise for room-temperature power generation and emerging cooling applications.

In summary, we demonstrated the remarkably high thermoelectric performance of non-Bi2Te3 module, consisting of n-type Mg3.2Bi1.5Sb0.498Te0.002Cu0.01 and p-type Mg0.99Cu0.01Ag0.97Sb0.99, for room-temperature power generation, high thermoelectric cooling. Herein, the n-type material's thermoelectric performance was maximized through rationally designing the microstructure by tuning the sintering temperature and minor Cu addition. The thermal grain-boundary resistance at the low-temperature range was completely eliminated that contributed to the record-high charge carrier mobility and thus significantly enhanced the electronic properties. Therefore, the achieved room-temperature ZT was boosted to 0.9, in addition to a broad temperature plateau above 1 from 323 to 423 K. Our work highlights the importance of microstructure on the charge carrier transport and, more importantly, offers great hope for room-temperature thermoelectric application using non-Bi2Te3 materials and devices.

Methods

Materials synthesis. High-purity raw materials from Sigma-Aldrich company were directly weighed according to the nominal composition Mg3.2Bi1.5Sb0.498Te0.002Cu0.01 or Mg1−xCu1Cu0.01, as well as Mg1−xCu1Ag0.97Sb0.99 (x = 0 and 0.01), loaded into the ball-milling jaw in the glovebox, and finally subjected to milling process (SPEx SamplePrep 8000 Mixer Mill). The ball-milled powder was directly subjected to sintering without a pre-calcination process. For Mg3.2Bi1.5Sb0.498Te0.002Cu0.01, the ball-milling time is 5 h and the obtained nanopowders were loaded into the graphite die and sintered by spark plasma sintering (SPS, SPS-1080 System, SPS SYNTEX INC) at different sintering temperatures (723, 873, 973, and 1073 K) with the pressure of ~60 MPa for 10 min. For Mg1−xCu1Cu0.01Ag0.97Sb0.99, we used the two-step ball-milling method and then did SPS at 573 K22,35.

Phase and microstructure characterizations. The phase structure was characterized by powder X-ray diffraction (XRD, SmartLab®Rigaku) with Cu Kα radiation. DSC measurement (Netzsch STA 449F1 Jupiter) was performed in an N2 atmosphere at a heating rate of 15 K/min. The microstructure and composition analysis were characterized using a field emission scanning electron microscope (FESEM, Hitachi S-4800) equipped with an energy dispersive spectrometer (EDS, Horiba EMAXEvolution X-Max).

Material property characterizations. Bar samples with a dimension of around 2.5 mm × 2.5 mm × 9 mm were cut from the pressed disks and used for simultaneous measurement of electrical resistivity (ρ) and Seebeck coefficient (S) on a commercial system (ULVAC ZEM-3). The thermal conductivity κtot was calculated using κtot = D/ρα, where D, ρ, and α are the thermal diffusivity, specific heat capacity, and density, respectively. The thermal diffusivity coefficient (D) and the specific heat capacity (Cp) were concurrently measured for the disk sample on a laser flash system (Netzsch LFA 467, Germany) with a pyroceram disk as a reference sample. For example, Cp measurement result of Mg3.2Bi1.5Sb0.498Te0.002Cu0.01 samples sintered at 973 K is in good consistency with the corrected Dulong–Petit law in this material system20 (Fig. S15). The sample density (d) was determined by the Archimedes method. The room-temperature Hall coefficient Rhi was measured using the PPMS (Physical Properties Measurement System, Quantum Design) with the AC transport option. The data were obtained with a magnetic field sweeping from −5 T to +5 T. The Hall carrier concentration (nH) was obtained by nH = 1/eRhi and the Hall carrier mobility (μH) was calculated by μH = eRH, where e is the electronic charge and σ the electrical conductivity. The above-mentioned measurement results are directly obtained from one sintering disk.

Module fabrication, performance measurement, and stimulation method. Thermoelectric legs of n-type Mg3.2Bi1.5Sb0.498Te0.002Cu0.01 and p-type Mg0.99Cu0.01Ag0.97Sb0.99, with interfacial layers were fabricated by the one-step SPS using the same condition as previously mentioned. Fe powder and Ag powder for n-type and p-type contact layer was used as the starting material, respectively. These obtained sandwich disks were grinding, polishing, and dicing. The cross-section of legs is 2.0 mm × 2.0 mm with a total length of 3 mm. The lengths of the thermoelectric elements and interfacial layer is 1.75 mm and 0.8 mm, respectively.

The power-generation performance measurement is similar to previous reports33,61. The eight-couple p- and n-type legs were alternately positioned onto the Cu substrate (18 mm × 15 mm × 1 mm), where thick Cu patterns were printed onto the heat-conducting polymer film. The legs were interconnected by Cu electrodes, in which InGa eutectic alloy was used for soldering. The power-generation performance was measured in a vacuum on a home-built apparatus with a hot-side temperature of 293, 313, 333, 353, and 373 K, in which the cold-side temperature was fixed at 278 K. The cold-side temperatures Tci and hot-side temperature Tfi were measured by using thermocouples embedded in the ceramic plates, respectively. A Cu block with known thermal conductivity (κcu) and a fixed cross-sectional area Acu was used to measure the heat flow. The heat flow out from the cold-side (Qout) was calculated based on Fourier's law:

\[ Q_{\text{out}} = k_{\text{cu}} \Delta T(A_{\text{cu}}/\rho_{\text{cu}}) \]

where \( k_{\text{cu}} \) is the vertical distance of Pt resistance thermometer in the Cu block and \( \Delta T \) is the temperature difference along the direction of heat flow. The conversion efficiency \( \eta \) was calculated using the following equation:

\[ \eta = \frac{P}{Q_{\text{in}} + Q_{\text{out}}} \]

where \( P \) is the electrical power output measured by a direct current electronic load.

The cooling-performance fabricated modules were measured keeping a hot-side temperature to be 373 K in a vacuum (10−7–10−3 Pa) on a home-built testing system. The setup is similar with that for power-generation measurement except that the hot- and cold-side is upside down and that the Cu block for evaluating heat flow is located above the module.

The three-dimensional finite-element simulations of power-generation and cooling performance was performed with COMSOL Multiphysics® software in the Heat Transfer Module. A geometrical model was built in the software interface to represent module with an identical geometry and dimension. The module structure from top to bottom is AlN ceramic 1 mm, graphite foil 0.1 mm, InGa layer 0.03 mm, thermoelectric element 3.35 mm, InGa layer 0.03 mm, Cu foil 0.21 mm, insulation foil 0.08 mm, grease 0.03 mm, and AlN ceramic 1 mm. Herein, the electrical and thermal contact resistances between these interfaces, as well as resistances of Cu electrodes are not considered in our simulation model. The measured temperature-dependent thermoelectric properties of n-type Mg3.2Bi1.5Sb0.498Te0.002Cu0.01 and p-type Mg0.99Cu0.01Ag0.97Sb0.99 were used for simulation, while those for the Ag and Fe contact layers were assumed to be constant.

Reporting summary. Further information on research design is available in the Nature Research Reporting Summary linked to this article.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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