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# Enhanced Thermoelectric Performance in Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> via Engineering Microstructure through Melt-Centrifugation

Melis Ozen,<sup>a,b</sup> Mujde Yahyaoglu,<sup>a,b</sup> Christophe Candolfi,<sup>c</sup> Igor Veremchuk,<sup>d</sup> Felix Kaiser,<sup>e</sup> Ulrich Burkhardt,<sup>e</sup>G. Jeffrey Snyder,<sup>f</sup> Yuri Grin,<sup>e</sup> and Umut Aydemir<sup>\*b,g</sup>

N-type Zintl phases with earth-abundant and non-toxic constituent elements have attracted intense research interest thanks to their high thermoelectric efficiencies in the mid-temperature range, exemplified by the recently discovered Mg<sub>3</sub>Sb<sub>2</sub> material. In this study, the liquid phase is expelled from the microstructure of the optimized *n*-type phase Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> by applying a melt-centrifugation technique leading to the formation of lattice dislocations, grain boundary dislocations and increasing porosity. Additional phonon scattering mechanisms were introduced in the microstructure through this manufacturing method, resulting in a significant 50% reduction in the total thermal conductivity from ~1 W m<sup>-1</sup> K<sup>-1</sup> to ~0.5 W m<sup>-1</sup> K<sup>-1</sup> at 723K. Combined with high power factors, this reduced heat transport leads to a dimensionless thermoelectric figure of merit, *zT*, value of ~1.64 at 723K, 43% higher than the value obtained in untreated Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> (*zT* ~1.14 at 723K). This peak *zT* value yields a predicted device *ZT* of 0.95, and a promising theoretical thermoelectric efficiency of about 12%. These results further underline the great potential of the lightweight Mg<sub>3</sub>Sb<sub>2</sub> material for mid-temperature energy harvesting via thermoelectric effects.

# 1. Introduction

Environmental concerns have been continually growing due to dramatic consequences (e.g., air pollution, global warming) of the utilization of non-renewable energy sources such as fossil fuels. Recent studies indicate that beyond 60% of the world's energy is lost mostly as a form of waste heat<sup>1</sup>. Therefore, harvesting waste heat is one of the promising options to support global energy sustainability. Thermoelectric materials, which directly convert heat into electricity or vice-versa, have sparked significant interest in energy generation and refrigeration applications. To improve the conversion efficiency of the thermoelectric devices, the dimensionless thermoelectric figure of merit of the materials, *zT*, defined as  $zT = \alpha^2 \sigma T / (\kappa_l + \kappa_e)$ should be enhanced. In this formula,  $\alpha$ ,  $\sigma$ ,  $\kappa_l$ ,  $\kappa_{e_l}$  and T represent the Seebeck coefficient, the electrical conductivity, the lattice thermal conductivity, the electronic thermal conductivity, and the absolute temperature, respectively<sup>2-4</sup>. As these transport

<sup>a.</sup> Graduate School of Sciences and Engineering, Koç University, Istanbul-34450, Turkey. properties are interdependent, achieving optimum zT values is challenging. Because tuning the electronic transport properties also affects the electronic contribution to the thermal conductivity, it is crucial to reduce the lattice thermal conductivity by phonon scattering without affecting the electronic properties of materials. In recent years, it has been demonstrated that the lattice thermal conductivity can be reduced by atomic scale issues, e.g. increasing complexity of chemical bonding or, on the mesoscale<sup>5</sup>, the wide range of phonon frequencies could be scattered by both dislocation scattering and phonon-pore interface scattering<sup>6-9</sup>.

Zintl phases can display high thermoelectric efficiencies stemming from their tunable electronic transport properties along with their inherently low lattice thermal conductivities<sup>10-</sup> <sup>12</sup>. Since their crystal structure is formed by a covalently-bonded network or units of complex anions together with ionically loosely-bonded electropositive cations, Zintl phases may be categorized as phonon-glass, electron-crystal (PGEC) systems <sup>13</sup>. So far, detailed investigations have been focused on various types of Zintl phases such as 0-dimensional (14-1-11)<sup>14, 15</sup>, 1dimensional (5-2-6, 3-1-3)<sup>16, 17</sup>, 2-dimensional (9-4-4, 1-2-2, 1-1-4)<sup>18, 19</sup> and 3-dimensional compounds (e.g., clathrates, skutterudites)<sup>20-25</sup>. Among those, several Zintl compounds such as Yb<sub>14</sub>MnSb<sub>11</sub><sup>14</sup>, Ca<sub>5</sub>Ga<sub>2</sub>As<sub>6</sub><sup>26</sup>, β-Zn<sub>4</sub>Sb<sub>3</sub><sup>27</sup>, BaGa<sub>2</sub>Sb<sub>2</sub><sup>28, 29</sup> Yb(Cd<sub>1</sub>-<sub>x</sub>Zn<sub>x</sub>)Sb<sub>2</sub><sup>30</sup>, EuZn<sub>2</sub>Sb<sub>2</sub><sup>31</sup> and Mg<sub>3</sub>Sb<sub>2</sub><sup>32, 33</sup> were found to be highlyefficient thermoelectric materials upon proper optimization of their carrier concentration. To date, most of the Zintl compounds display persistently p-type semiconducting behavior because of intrinsic cation vacancies. However, recent computational studies indicate that n-type Zintl phases may

<sup>&</sup>lt;sup>b.</sup> Koç University Boron and Advanced Materials Application and Research Center, Istanbul-34450, Turkey.

<sup>&</sup>lt;sup>c.</sup> Institut Jean Lamour, Université de Lorraine Nancy Cedex-54011, France

<sup>&</sup>lt;sup>d.</sup> Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany

e. Max Planck Institute f
ür Chemische Physik Fester Stoffe, Dresden-01187, Germany.

f. Department of Materials Science and Engineering, Northwestern University, Evanston, IL-60208, USA

<sup>&</sup>lt;sup>g.</sup> Department of Chemistry, Koç University, Sariyer, Istanbul, 34450, Turkey.

<sup>&</sup>lt;sup>+</sup> Footnotes relating to the title and/or authors should appear here.

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exhibit higher thermoelectric performances compared to their p-type counterparts<sup>34-38</sup>.

This last prediction has been verified experimentally for the low-cost, non-toxic Mg<sub>3</sub>Sb<sub>2</sub> Zintl phase.<sup>39</sup> Mg<sub>3</sub>Sb<sub>2</sub> crystallizes in the inverse  $\alpha$ -La<sub>2</sub>O<sub>3</sub> structure type described in the trigonal space group  $P\overline{3}m1$ . The crystal structure consists of an anionic [Mg<sub>2</sub>Sb<sub>2</sub>]<sup>2-</sup> layer formed by tetrahedrally coordinated Mg with Sb atoms, and an electron donating cationic Mg<sup>2+</sup> layer at the octahedral sites inserted between two anionic [Mg<sub>2</sub>Sb<sub>2</sub>]<sup>2-</sup> units as shown in Fig. 1 <sup>40, 41</sup>. While the [Mg<sub>2</sub>Sb<sub>2</sub>]<sup>2-</sup> layers provide high hole mobility, the Mg<sup>2+</sup> cations are responsible for the good electronic tunability along with low lattice thermal conductivity. We would like to note that Mg<sub>3</sub>Sb<sub>2</sub> displays isotropic thermoelectric properties, which Zhang et al. ascribed to three-dimensional bonding network —as opposed to a layer-structure— with the interlayer and intralayer bonds having similar ionic character <sup>38</sup>.

Because of Mg's high vapor pressure and reactivity, Mg vacancies that act as electron acceptors are formed during the synthesis steps. The resulting shift of the chemical potential towards the valence bands leads to a p-type conduction behaviour<sup>32, 33, 36</sup>. Recently, Tamaki et al. have successfully synthesized *n*-type Mg<sub>3</sub>Sb<sub>2</sub> by suppressing the formation of Mg vacancies using an excess amount of Mg in the nominal composition<sup>32</sup>. Remarkably, the subsequent optimization of the thermoelectric properties led to very high zT values ~1.5 near 800 K, outperforming the canonical p-type thermoelectric Zintl phase Yb<sub>14</sub>MnSb<sub>11</sub>. Following this first report, many research groups have devoted enormous attention to further improving the thermoelectric properties of *n*-type Mg<sub>3</sub>Sb<sub>2</sub>-based materials through various strategies such as band engineering, orbital engineering, scattering mechanism carrier tuning. concentration optimization, annealing under Mg-rich atmosphere, grain size optimization etc.<sup>36, 40-52</sup>.



**Fig. 1** a) The crystal structure of  $Mg_3Sb_2$  with  $[Mg_{22}Sb_2]^{2-}$  anionic substructure,  $Mg1^{2+}$  cationic sheet and the ionic interaction between them. b) Almost perfect octahedral coordination of Mg1 with six equal Mg1-Sb bonds. c) Slightly distorted tetrahedral coordination of Mg2 with three long and one short Mg2-Sb bonds.

Here, we illustrate the effectiveness of microstructure engineering in refining the thermoelectric properties of *n*-type Mg<sub>3</sub>Sb<sub>2</sub>, adding a novel strategy to the arsenal mentioned above. This approach is based on squeezing out the excess melt-centrifugation liauid applying the technique, demonstrated for the (Bi,Sb)<sub>2</sub>Te<sub>3</sub> thermoelectric material<sup>9</sup>. In this study, Pan et al. showed that melt-centrifugation generates lattice and grain boundary dislocations and increases the degree of porosity. Both features open novel sources of phonon scattering, which result in reduced lattice thermal conductivity and hence, increased zT. Herein, the effects of this technique on the microstructure and transport properties of the optimized nstarting composition type Mg<sub>3.2</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> were investigated for the first time. In this study, an excess amount of low-melting element Mg is added to the target composition to achieve eutectic mixtures. Through the centrifugal force, the liquid phase is removed from the microstructure forming dislocation arrays and porosity (See Fig. 2). The best sample displays significantly low lattice thermal conductivity (~0.33 Wm<sup>-1</sup>K<sup>-1</sup>) with a high zT value of around 1.64 at 723 K, which is higher than that achieved in this study without melt centrifugation (1.14 at 723 K) and other studies reported for  $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$  (*zT* ~1.5 at 723 K) <sup>32, 34, 53-57</sup>.

#### 2. Experimental

## 2.1. Sample Preparation

High-purity magnesium powder (Mg, 99.8%; Alfa Aesar), bismuth pieces (Bi, 99.999%; Alfa Aesar), antimony shots (Sb, 99.999%; Alfa Aesar) and tellurium pieces (Te, 99.9999%; Alfa Aesar) were used as starting elements. To prevent undesired reactions during high-energy ball milling because of the high reactivity of materials, all sample handling processes were carried out in an Ar-filled glovebox. Stoichiometric mixtures of elements were loaded into a stainless-steel vial with two halfinch stainless-steel balls and sealed in the glove box. The parent compounds with nominal compositions of Mg<sub>3.2</sub>Sb<sub>2</sub> and Mg<sub>3.2</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> (MSBT), were produced through mechanical alloying for two hours using a high energy mill (SPEX 8000M Mixer/Mill, 1425 rpm). Subsequently, the resulting powders were loaded into a graphite die and consolidated by spark plasma sintering (SPS) for 10 minutes at 823 K under a



**Fig. 2** a) Schematic view of melt-centrifugation apparatus, b) sample in quartz tube before melt-centrifugation, c) sample in quartz tube after melt-centrifugation, d) side and top view of the samples after melt centrifugation process.

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uniaxial pressure of 50 MPa. For the melt-centrifugation experiments, two different preparation conditions were applied regarding the amount of excess Mg and the way of its addition. For the first case, the raw materials with an excess amount of Mg (46 wt.%) were weighed and added to the vial. The highenergy ball milling was then conducted for 2 h, yielding to the MSBT\_46in\_30m\_c sample. For the second case, the main MSBT composition was produced using the above-written route. Afterward, excess amounts of Mg (46 wt.% and 20 wt.%) were externally added to 5 g of this pre-reacted sample, and further ball milled for an extra 30 minutes. The same sintering process was applied for this sample. Following SPS, MSBT pellets were sealed under vacuum in a quartz ampoule with quartz wool placed on either side of the pellets (see Fig. 2). Before melt centrifugation, the sample was containing both Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> and Mg phases according to the X-ray diffraction pattern (see Sec. 3.1). Afterward, the sealed ampoules were undergone heat treatment at 750°C for two different time periods of 30 minutes and one hour. The heat treatment temperature was selected between the melting points of the Zintl phase and the eutectic point. After the heat treatment, the quartz ampoules were inserted quickly (in ca. 3 seconds) to the centrifuge (Megafuge 8). During the centrifugation process, quartz wools were placed inside the swinging-buckets and the samples were centrifuged for 2 minutes at the speed of 3900 rpm (Fig. 2). Due to the centrifugal force, the randomly distributed liquid phase was squeezed out of the bulk sample to the surface of the quartz ampoules. The as-prepared samples will be hereafter labelled as MSBT\_46ext\_30m\_c, MSBT\_20ext\_30m\_c and MSBT\_20ext\_1h\_c. Labeling the samples with "ext" and "in" indicates the synthesis method used, that is, with external or insitu Mg addition. The heat treatment durations for the centrifuged samples are indicated as 30m or 1h. Lastly, "c" letter at the end of the labels is used for centrifuged samples.

#### 2.2. Sample Characterization

The crystal structure and the phase purity of the samples were determined by room-temperature X-ray diffraction (XRD, Rigaku Mini Flex 600) with Cu  $K_{\alpha 1}$  ( $\lambda = 1.5406$  Å) radiation (40 kV voltage and 15 mA). The lattice parameters were refined, and texture analysis was performed by using the WinCSD program<sup>58</sup>. To analyze the microstructure and the chemical composition, Scanning Electron Microscopy (SEM) with Energy Dispersive Xray Spectroscopy (EDS) analyses were carried out using a Zeiss Ultra Plus Field Emission Scanning Electron Microscope. SEM images were obtained by etching the surfaces with dilute nitric acid (1 M) for 10 sec. Also, more accurate chemical composition analysis was conducted with wavelength dispersive X-ray spectroscopy (WDS) on an electron microprobe (Cameca SX 100, tungsten cathode) using the line compound Mg<sub>2</sub>Si and certificated pure elements Sb, Bi and Te as references. . The observation of dislocation arrays and grain boundary dislocations inside the microstructure was performed by Transmission Electron Microscopy (TEM) images using a Hitachi Field Emission Transmission Electron Microscope HF5000 instrument operated at 200 kV. Transmission electron microscope (TEM) images of MSBT sample without meltcentrifugation were recorded on a Hitachi HT7700 TEM instrument operated at 120 kV at Koc University.

#### 2.3. Transport Properties Measurements

All the transport properties were measured between 323 and 723 K. Thermal diffusivity, D, was measured on disc-shaped samples (10 mm in diameter) with a Netzsch LFA 467 laser flash apparatus. The thermal conductivity was calculated using the relation  $k = D \times C_p \times d$ , where  $C_p$  is the heat capacity, and d is the experimental density. The density of the samples was determined by measuring weight and geometrical dimensions. C<sub>p</sub> was calculated by the Maier-Kelley polynomial expression  $(C_p = \frac{3NR}{M_w}(1 + 1.3 imes 10^{-4}T - 4 imes 10^3T^{-2})$ , between 323 and 723 K (See Fig. S1) <sup>59</sup>. The electronic thermal conductivity  $\kappa_e$  was calculated through the Wiedemann-Franz law  $\kappa_e = L\sigma T$ , where L is the Lorenz number and  $\sigma$  is the electrical conductivity. The Lorenz numbers were calculated for each sample through the  $\frac{L}{10^{-8}W\Omega K^{-2}} = 1.5 + \exp\left(\frac{-|a|}{116\mu V/K}\right),$ relation, where  $\alpha$  is measured in  $\mu V/K^{60}$ .

Seebeck coefficient and electrical resistivity measurements were performed using an ULVAC ZEM-3 system. For these measurements, samples were cut into rectangular bars using a low-speed diamond-wire saw (MTI-SYJ-150). Of note, the LFA and ZEM-3 measurements were all performed parallel to the SPS pressing direction. The measurements for the bestperforming *zT* material were conducted on pieces cut perpendicular to the pressing direction as well.

The thermoelectric device figure of merit, *ZT*, value and the maximum efficiency,  $\eta$ , were calculated by using a spreadsheet supplied in the the study of Snyder et al.<sup>61</sup> Basically, *ZT* value for a specific temperature difference  $\Delta T = T_h - T_c$  was calculated with  $ZT = \left(\frac{T_h - T_c(1-\eta)}{T_h(1-\eta) - T_c}\right)^2$  by using maximum efficiency,  $\eta$ , determined between hot and cold side temperatures through temperature dependent *S*(*T*),  $\rho(T)$ , and  $\kappa(T)$ . For further details see Ref. 61.

# 3. Results and Discussion

#### 3.1. Phase and Crystal Structure Analysis

As depicted in the phase diagram of  $Mg_3Sb_2$  (Fig. S2), Mg excess phase (65 at-% Mg) melts around 750°C (eutectic temperature ~627°C) and dissolves a small amount of  $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}$ . During the melt centrifugation, a fraction of the liquid phase is removed from the bulk sample through the walls of the quartz ampoule, and almost phase-pure and porous  $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}$  can be obtained. Fig. 3 presents the XRD results of the SPS treated samples  $Mg_{3+x}Sb_2$ , MSBT, MSBT\_20ext\_1h and MSBT\_20ext\_1h\_c. For all samples, the reflections of the main phase can be well indexed by the trigonal



Fig. 3 XRD patterns (Cu-K  $\alpha$  radiation) of Mg\_3+xSb\_2, MSBT (black), MSBT\_20ext\_1h (pink) and MSBT\_20ext\_1h\_c (green).

 $Mg_3Sb_2$  crystal structure ( $P\overline{3}m1$  space group). XRD measurements demonstrate that  $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}$  (MSBT) was produced as a pure phase. The sample MSBT\_20ext\_1h shows additional reflections that correspond to elemental Mg. After the centrifugation process, only the Zintl phase was observed within the detection limits of XRD. The rest of the centrifuged samples also displayed similar results with the MSBT\_20ext\_1h sample before and after the centrifugation process (See Fig. S3). The EDS elemental mapping analyses performed on MSBT\_20ext\_30m\_c and MSBT\_20ext\_1h\_c samples show Mg and Bi excess grains within the microstructure (see Fig. S4).

The refined lattice parameters of the samples are tabulated in Table S1. The MSBT sample has lattice parameters very similar to those published for single-crystalline Mg<sub>3</sub>Sb<sub>2</sub><sup>62</sup>. The substitution of Bi3- for Sb3- leads to slightly higher lattice parameters for the MSBT sample due to the larger ionic radii of Bi<sup>3-</sup> (1.93 Å) compared to Sb<sup>3-</sup> (1.88 Å)<sup>63</sup>. After applying centrifugation followed by 30 and 60 min of annealing, the lattice parameters were increased slightly, suggesting a tiny change in the sample's chemical composition. Based on the Rietveld refinements conducted on MSBT\_20ext\_1h and MSBT 20ext 1h c samples, no pronounced texturing was observed for both samples (See Fig. S5 and S6). This agrees with the theoretical calculations demonstrating Mg<sub>3</sub>Sb<sub>2</sub> has isotropic chemical bonding and transport properties<sup>38, 64, 65</sup>. The experimental studies carried out by Imasato et al., Tamaki et al., and Xin et al. manifest that  $\mathsf{Mg}_3\mathsf{Sb}_2$  displays isotropic thermal conductivity behavior, while the experimental electronic transport data given by Song et al. and Lv et al. show that there is no reasonable difference in transport properties measured in different directions<sup>32, 62, 66-68</sup>.

The composition of the MSBT was determined by WDXS analysis by averaging the results of 10 different, randomly-chosen spots as  $Mg_{3.08(1)}Sb_{1.44(2)}Bi_{0.47(1)}Te_{0.01(3)}$ , which points to similar stoichiometry as the nominal composition (SI Table S2 and Fig. S7).

#### 3.2. Microstructure Analysis

Microstructure examinations were performed by SEM and TEM. Several TEM studies have been previously conducted on Mg<sub>3</sub>Sb<sub>2</sub>-based materials synthesized by mechanical alloying <sup>51,</sup> <sup>54, 69-71</sup>. To the best of our knowledge, none of the studied samples present lattice dislocations or ordered grain boundaries in the microstructures. TEM images shown in Fig. 4 for MSBT sample indicates that mechanical alloying technique without additional synthetic treatments (e.g., melt centrifugation) does not tend to form lattice dislocations or ordered grain boundaries. In Fig. 5a and 5b, SEM images of the samples MSBT\_20ext\_30m\_c and MSBT\_20ext\_1h\_c show that porosities with various sizes emerged after the centrifugation process. Therefore, to further investigate the microstructural effects of melt-centrifugation; TEM images of MSBT\_20ext\_30m\_c are shown from different two perspectives, one from out-of-plane direction (Fig. 5c; parallel to the sintering direction) and the other from the in-plane direction (Fig. 5d; perpendicular to the sintering direction). Distinctly ordered grain boundary dislocations were observed from both in-plane and out-of-plane directions owing to the centrifugal force (For large and more distinct images see Fig. S8). Besides, lattice dislocations and dislocation arrays within the grains were identified in both directions. The removal of the liquid eutectic phase under strong centrifugal force induces grain rotations and misfits in the microstructure. These large



Fig. 4 TEM images of MSBT sample without melt-centrifugation.



Fig. 5 SE (Secondary Electron) images (5 kV and 20 kV HV) of melt-centrifuged samples a) MSBT\_20ext\_30m\_c b) MSBT\_20ext\_1h\_c, and TEM images of MSBT\_20ext\_30m\_c c) taken from out-plane direction and d) taken from inplane direction

grain misfits are accommodated by the formation of lattice dislocations. In addition, during the uniaxial melt centrifugation, liquid eutectic phase penetrates through the grain boundaries resulting in much higher diffusion length for the atoms and the dislocations at the grain boundaries. This effect is considered as the main reason for the formation of ordered grain boundaries. As dislocations generate strain fields and act as an additional source of phonon diffusion, their presence may prevent phonon propagation and reduce the lattice thermal conductivity<sup>6, 9, 72, 73</sup>.

#### 3.3. Electronic Transport

As shown by Imasato et. al. and Shuai et. al., the excess Mg in Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> can deteriorate the electronic transport properties<sup>54, 55</sup>. The addition of 46 wt.% excess amount of Mg decreases the electrical resistivity values, due to the additional electrons provided. The electrical resistivity values of the sample with an external addition of the same amount of Mg (MSBT 46ext 30m c) are similar to those of the noncentrifuged sample. This lack of difference might be related to lower Mg concentration in the crystal structure comparing with internally Mg added samples, suggesting that the external addition facilitates the removal of excess Mg.

By decreasing the excess amount of Mg from 46 wt.% to 20 wt.%, the electrical resistivity increases substantially after centrifugation. Both the formation of porosity and the lower amount of Mg might explain this behavior. As observed in Fig. 6a, increasing the heat treatment time from 30 min to 1h leads to a decrease in the electrical resistivity for the sample MSBT 20ext 1h c compared to MSBT 20ext 30m c. This behavior is likely associated with grain-boundary dominated charge transport. As grains act as two different phases at the grain boundaries, a potential barrier is generated along the grain boundary resulting in higher electrical resistivity<sup>43, 48</sup>. As shown in Fig. S9, different heat treatments lead to different microstructural features. When the annealing time is increased from 30 min. to 1 h, the removal of liquid phase from the



Fig. 6 a)The electrical resistivity, b) Seebeck coefficient of Mg<sub>3+x</sub>Sb<sub>2</sub>, MSBT(black), MSBT\_46in\_30m\_c (red), MSBT\_46ext\_30m\_c (blue), MSBT\_20ext\_30m\_c (pink) and MSBT\_20ext\_1h\_c (green) as a function of temperature, c) weighted mobility data as a function of temperature and d) weighted mobility as a function of density data of MSBT\_20ext\_30m\_c (pink) and MSBT\_20ext\_1h\_c (green) compared to the literature data 32, 46, 54, 57

microstructure through centrifugation results in more homogeneously-distributed porosity for MSBT\_20ext\_1h\_c compared to MSBT\_20ext\_30m\_c sample. In addition, Fig. S10 highlights the differences between the grain structure of these samples. While MSBT\_20ext\_30m\_c sample has almost welldefined grain boundaries, MSBT\_20ext\_1h\_c sample demonstrates more fused grains and semicoherent grain boundaries as shown by residual neck formation. As discussed by Kim et al., semicoherent grain boundaries has less of an effect on electron scattering while inducing enough strain for significant phonon scattering <sup>6</sup>. Therefore, the presence of semicoherent grain boundaries explains the higher mobility and lower electrical resistivity in the MSBT\_20ext\_1h\_c sample compared to MSBT\_20ext\_30m\_c sample.

Both the MSBT\_46in\_30m\_c and MSBT\_46ext\_30m\_c samples have very small negative values of the Seebeck coefficients (Fig. 6b) compared to the reference compound  $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}$  (MSBT). These results are in accord with the trend observed in the electrical resistivity values, indicative of significant reduction in the electron concentration. On the other hand, with 20 wt.% Mg addition, the Seebeck coefficients of MSBT\_20ext\_1h\_c and MSBT\_20ext\_30m\_c are almost identical to that of the non-centrifuged MSBT sample at higher temperatures. Large, negative Seebeck coefficients observed for those. The high-temperature heat treatment applied before centrifugation might result in Te loss along with Mg. However, due to the very small amount of Te in the composition, it is hard to detect this change by chemical analyses. Besides, the similar Seebeck coefficients of the MSBT\_20ext\_1h\_c and MSBT\_20ext\_30m\_c samples promote the idea that the difference observed in the  $\rho$  values are due to grain-boundarydominated charge transport, in which its influence on the Seebeck coefficient is negligible.

The weighted mobilities of the samples were calculated from the measured electrical conductivity and Seebeck coefficient data using a Drude–Sommerfeld free electron model approximation<sup>74</sup>. The weighted mobility is independent of the position of the chemical potential and hence, of the carrier concentration. It provides valuable information about the power factor as well as zT, provided that the carrier concentration is optimized, and about the intrinsic properties of the charge carriers, grain boundary resistance, charge transport mechanisms with more accurate temperature dependence <sup>43,</sup> <sup>74</sup>. The weighted mobility values of centrifuged samples are reported in Fig. S11. Compared to the estimated weighted mobility data counting the grain boundary resistance and bipolar effects (See Ref. 40), the weighted mobilities of the centrifuged samples are more affected by the grain boundary resistance74. Therefore, the weighted mobility values of the  $MSBT\_20ext\_1h\_c \ and \ MSBT\_20ext\_30m\_c \ samples \ are$ presented in Fig. 6d at 573K to eliminate this effect. The relatively low weighted mobility values compared to MSBT sample and the literature might arise from the low average distance between the scattering centers, which are analogous to the electron mean free path<sup>75</sup>. Also, the lower density (86.6% and 85.3%) of MSBT\_20ext\_1h\_c and MSBT\_20ext\_30m\_c that emerged in the microstructure due to the porosities results in significantly low weighted mobilities; being in an agreement with the study conducted by Witting et. al<sup>76</sup>. As seen in Fig. 6d, increasing the annealing time suppresses the negative effect of the scattering centers which mentioned in the electrical resistivity discussion, leading to higher weighted mobility values.

#### 3.4. Thermal Transport

The total thermal conductivity  $\kappa$  of the different samples is presented in Fig. 7a. The lattice thermal conductivity values  $\kappa_{l}$ , shown in Fig. 7b, were obtained by subtracting  $\kappa_e$  from  $\kappa$ . Despite the decrease in the density of the MSBT\_46in\_30m\_c sample,  $\kappa$  is higher at high temperature. This behavior is related to minority carrier effects that result in an additional bipolar contribution to  $\kappa$ . In line with the electrical resistivity and Seebeck coefficient data, the  $\kappa_e$  values of MSBT\_46in\_30m\_c increase with increasing temperature much faster than the concomitant decrease in  $\kappa_l$ .

For the samples MSBT 20ext 1h c and MSBT\_20ext\_30m\_c,  $\kappa_e$  was not affected significantly by the centrifugation process (See Fig. S12). In contrast, as seen in Fig. 5 and Fig. S8, grain boundary and lattice dislocations impede the propagation of phonons and result in a significant decrease in  $\kappa_l$ as high as 56-60% (Fig. 7b). This behavior is analogous with the melt-centrifugation study on Bi<sub>0.3</sub>Sb<sub>1.7</sub>Te<sub>3</sub>, in which a reduction in  $\kappa_l$  of around 60% was reported due to the formation of pores, dislocation strains, and interfaces. The effects of two different phases (air in pores and the main Mg<sub>3</sub>Sb<sub>2</sub> phase) on the thermal conductivity has been analyzed using the effective medium theory (EMT) with the relation  $\kappa_{l,p} = \kappa_{l,d} f_{\kappa}(\varepsilon)$ , where  $f_{\kappa}(\varepsilon) =$  $(1-3\varepsilon/2)$  and  $\varepsilon$  is the volume fraction of porosity<sup>9</sup>. Using porosity of centrifuged samples of  $\varepsilon \sim 0.14$ , EMT results in a  $\kappa_{l,p}/\kappa_{l,d}$  of around 0.78, indicating that the porous structure leads to ~22% reduction in lattice thermal conductivity, with the extra reduction stemming from other phonon scattering mechanisms, e.g., dislocation strain scattering. Compared with the measured lattice thermal conductivity data from the literature, MSBT\_20ext\_1h\_c and MSBT\_20ext\_30m\_c present very low lattice thermal conductivity (0.50 to 0.33 Wm<sup>-1</sup>K<sup>-1</sup> between 323-723 K) and total thermal conductivity (0.55 to 0.48 Wm<sup>-1</sup>K<sup>-1</sup> between 323-723 K) for all temperature range, with a remarkable difference of around 38-50 % 32, 34, 46, 52, 54-57.

While the defects and grain boundaries in the microstructure are detrimental to the electrical conduction, different types of dislocations and porosity formation additionally diminish the thermal conductivity by creating phonon scattering mechanisms covering a broader frequency range of the phonon spectrum. This beneficial influence becomes more apparent for the MSBT\_20ext\_1h\_c and MSBT\_20ext\_30m\_c samples.

As discussed for the electrical transport properties of these samples, MSBT\_20ext\_30m\_c shows higher electrical resistivity values than MSBT\_20ext\_1h\_c does; likewise, the electronic thermal conductivity values of them are similar. The comparison of these two samples, one annealed for 30 min. and the other one for 1 hour, reveals a homogenous distribution of a)

F.

b)

2

#### Journal Name

porosity in the latter case (Fig. S9a and S9c). This behavior can also be correlated to semicoherent grain boundaries observed in MSBT\_20ext\_1h\_c (Fig. S10) for higher temperature and annealing time, implying that, although the chemical composition did not change appreciably, the distance between the scattering centers have increased for the latter sample. Therefore, a decrease in the electrical resistivity and an increase in weighted mobility are observed for this sample. This led to slightly higher  $\kappa_e$  value for MSBT\_20ext\_1h\_c , which was compensated by lower  $\kappa_l$  as a consequence of the porosity difference(volume fraction of 13.5% vs 14.7%). Finally, compared to the MSBT sample without centrifugation, lower electronic thermal conductivity combines with stronger phonon scattering, resulting in total thermal conductivity values that decrease by more than 50% for centrifuged samples, as illustrated in Fig. 7a.

### 3.5. Thermoelectric Figure of Merit

Fig. 8a shows the temperature dependence of the thermoelectric figure of merit zT for centrifuged and noncentrifuged samples. The results evidence that the addition of 46 wt.% Mg negatively affects the zT values for both in-situ and external addition to the main composition. On the other hand, an addition of only 20 wt.% Mg successfully augments the zT values over the entire temperature range with respect to  $Mg_{3+x}Sb_{1.5}Bi_{0.49}Te_{0.01}. \ \ The \ \ dramatic \ \ reduction \ \ in \ \ thermal$ conductivity is the main ingredient yielding higher *zT* values. Higher zT is directly correlated with a higher quality factor,  $B \propto$  $\mu_w/\kappa_l$ ; for this reason, higher weighted mobility is needed for an efficient thermoelectric material together with low lattice thermal conductivity 40, 43. As mentioned above, the presence of different scattering mechanisms due to the peculiar microstructure affects both the thermal and electronic properties. In this regard, quality factor determination is essential to assess the net gain from melt-centrifugation, independently from variations in the carrier concentration. The comparison of the quality factors of MSBT sample (B = 89) and the centrifuged ones, MSBT\_20ext\_30m\_c (B = 133), and MSBT 20ext 1h c (B = 185), evidences a clear effect of meltcentrifugation. Although the MSBT sample has a higher weighted mobility value, the centrifuged samples present higher quality factors due to much lower  $\kappa_l$  values achieved. This may indicate that pore-interface and dislocation scattering is more effective in reducing thermal conductivity than electrical conductivity because of larger mean free paths of phonons compared to those of the charge carriers. With such hierarchical microstructure comprising semicoherent grain boundaries, an overall enhancement in zT for the melt-centrifuged samples is achieved 9. With longer heat treatment times and centrifugation, a peak zT of ~1.64 was achieved for this sample, corresponding to an enhancement of around 43% compared to that of the MSBT sample without applying any carrier concentration optimization method. Moreover, the highest zT achieved in this study is nearly 10 % higher than those reported for *n*-type  $Mg_{3.2}Sb_{1.5}Bi_{0.49}Te_{0.01}$  (nominal composition) with *zT* of

~1.5<sup>32, 34, 53-57</sup> at 723 K, and comparable to the best reported *zT* values achieved with different doping strategies (See Fig. S15) <sup>55-57, 71, 75</sup>. As depicted in Fig 8b, the device *ZT* value of the best-performing sample (MSBT\_20ext\_1h\_c) was calculated to be 0.95 at 723 K, which corresponds to a theoretical maximum efficiency value of around 12 %.

## 4. Conclusions

A microstructure engineering strategy based on meltcentrifugation was successfully implemented to the *n*-type Zintl phase Mg<sub>3+x</sub>Sb<sub>1.5</sub>Bi<sub>0.49</sub>Te<sub>0.01</sub> for the first time. This technique not only creates lattice and grain boundary dislocations but also a porous microstructure. By annealing at 750°C for one hour before the melt centrifugation, the electronic transport properties of the MSBT\_20ext\_1h\_c sample were enhanced compared to those of the MSBT\_20ext\_30m\_c sample annealed for only 30 minutes. As a result, although the power factor decreased by ~30% compared to noncentrifuged sample, a marked drop in the thermal conductivity of around 50% led to enhanced zT values thanks to melt-centrifugation. The total thermal conductivity was reduced by 50 % from 1 W m<sup>-1</sup> K<sup>-1</sup> to  ${\sim}0.5~W~m^{\text{-1}}~K^{\text{-1}}$  at 723 K for the MSBT\_20ext\_1h\_c sample. samples MSBT\_20ext\_1h\_c Additionally, the and MSBT\_20ext\_30m\_c display increased *zT* values over the entire temperature range. Regarding the MSBT\_20ext\_1h\_c sample, the highest zT value increases from 1.14 to 1.64 at 723K which signifies an enhancement of almost 43%. The hierarchical microstructure and well fused grains leads to an overall enhancement in zT for the melt-centrifuged samples. Besides, with a calculated device ZT value of 0.95, a promising theoretical efficiency of approximately 12% is predicted for this sample (Fig 7b.). Our results further underline the strong potential of the lightweight Zintl phase Mg<sub>3</sub>Sb<sub>2</sub> for midtemperature thermoelectric applications in power generation. This work elaborately demonstrates that high thermoelectric efficiency can be achieved in porous, lightweight thermoelectric materials through the melt-centrifugation technique.

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# **Conflicts of interest**

There are no conflicts to declare.

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