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RESEARCH ARTICLE

NANOCRYSTALLINE BI_2TE_3 VIA MECHANICAL ALLOYING: EFFECTS OF MILLING SPEED, PROCESS CONTROL AGENTS AND THERMOELECTRIC PERFORMANCE

Nurkhaizan Zulkepli[1], Jumril Yunas[2], Mohd Ambri Mohamed[2], Dedi[3], Mohammad Dani Al Qori[4], Mohamad Shukri Sirat[5], Azrul Azlan Hamzah[2,*]

[1]Centre of Foundation Studies, Universiti Teknologi MARA Cawangan Selangor, Kampus Dengkil, 43800 Dengkil, Selangor, Malaysia.
[2]Institute of Microengineering and Nanoelectronic (IMEN), Universiti Kebangsaan Malaysia (UKM) 46300 Bangi,Selangor, Malaysia.
[3]Research Center for Electronics, National Research and Innovation Agency, Bandung, Indonesia.
[4]Faculty of Mathematics and Natural Sciences, Institut Teknologi Bandung, Bandung, Indonesia.
[5]Malaysia Genome and Vaccine Institute, National Institutes of Biotechnology Malaysia, Jalan Bangi, 43000 Kajang, Selangor, Malaysia.

Abstract. Nanostructured thermoelectric materials have attracted considerable attention as a pathway to enhance device efficiency by reducing lattice thermal conductivity while maintaining favorable electrical transport. In this work, nanocrystalline Bi_2Te_3 was synthesized through mechanical alloying, with systematic evaluation of the effects of milling speed and the introduction of ethanol as a process control agent. Particle size analysis revealed that higher milling speeds promoted significant refinement, with optimal conditions achieved at 600 rpm, though further increases resulted in diminished efficiency due to particle agglomeration and heat generation within the milling vial. The incorporation of ethanol effectively reduced cold welding and particle clustering, yielding finer distributions; however, this came at the expense of powder yield, underscoring the trade-off between structural control and processing efficiency. Microstructural characterization using FESEM confirmed the transformation of bulk Bi_2Te_3 into nanograins with sizes approaching the sub-micron range, accompanied by agglomerated morphologies. Thermal conductivity measurements demonstrated a pronounced reduction for the milled samples compared with unmilled counterparts, a consequence of enhanced phonon scattering at grain boundaries. Importantly, electrical transport properties remained largely preserved, leading to an overall improvement in the thermoelectric figure of merit (ZT). These findings establish mechanical alloying as a cost-effective and scalable strategy to optimize Bi_2Te_3 for thermoelectric applications, particularly in waste heat recovery, low-temperature cooling, and portable energy systems, where efficiency, manufacturability, and scalability are critical.

Keywords: Nanocrystalline, bismuth telluride, thermoelectric, mechanical alloying, ball mill speed.

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***Corresponding author: azlanhamzah@ukm.edu.my**

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1. INTRODUCTION

Thermoelectric materials, which can directly convert heat into electricity, have become increasingly significant due to their potential applications in energy harvesting and waste heat recovery [1]. Among these materials, bismuth telluride (Bi_2Te_3) and its alloys are particularly favoured. However, despite their promising characteristics, the thermoelectric performance of Bi_2Te_3 is hindered by high thermal conductivity, k which limits the figure of merit (ZT) of these materials [2]. To improve their efficiency, various strategies, such as doping, nanostructuring [3], and mechanical alloying [4], have been employed to simultaneously reduce thermal conductivity while enhancing electrical conductivity. Notably, nanostructuring Bi_2Te_3 has proven to be effective in lowering lattice thermal conductivity through enhanced phonon scattering, while maintaining favourable charge carrier mobility [5].

The application of mechanical alloying has emerged as a promising method for synthesising nanostructured Bi_2Te_3. By subjecting a powder mixture of bismuth and tellurium to high-energy ball milling, this technique promotes the formation of Bi_2Te_3 with significantly reduced crystallite sizes, thus improving the thermoelectric performance. Zakeri et al. [5] demonstrated that high-energy ball milling reduced the particle size to approximately 9-10 nm, enhancing the thermoelectric properties of the material. Furthermore, Gharsallah et al. [6] utilised arc-melting to produce nanostructured Bi_2Te_3, achieving a figure of merit (ZT) of 0.6 at room temperature. These findings underline the efficacy of mechanical alloying in improving the thermoelectric performance of Bi_2Te_3 through nanostructuring. In addition, mechanical alloying has been found to aid in the formation of single-phase Bi_2Te_3, which exhibits superior thermoelectric properties due to the increase in interfaces within the material, leading to better phonon scattering and lower thermal conductivity.

In recent years, studies have also emphasised the importance of optimising milling parameters, such as milling time, ball-to-powder ratio [7], and milling speed [8], to further enhance the properties of nanocrystalline Bi_2Te_3. Robinson [9] investigated the effects of these parameters on the thermoelectric properties of Bi_2Te_3 alloys, revealing that an optimal milling time of 10 hours and a ball-to-powder ratio of 10:1 led to an increased ZT value for both n-type and p-type Bi_2Te_3. The study demonstrated that these parameters significantly affect the electrical conductivity and thermal conductivity of Bi_2Te_3, both of which are critical for improving thermoelectric performance. Moreover, the incorporation of process control agents (PCAs) during mechanical alloying has been shown to influence the microstructure and thermoelectric properties of Bi_2Te_3. Madavali et al. [10] demonstrated that using stearic acid as a PCA resulted in a reduction of thermal conductivity by 19 %, although it also led to a decrease in electrical conductivity due to the formation of insulating phases. This highlights the trade-off involved in optimising PCA content, which is crucial for achieving a balance between electrical and thermal properties to maximise the thermoelectric efficiency of the material.

While prior studies have investigated the influence of milling time, ball-to-powder ratio, and process conditions on Bi_2Te_3 refinement and thermoelectric properties, the role of milling speed and the trade-offs introduced by process control agents (PCAs) has not been systematically addressed. Milling speed directly governs collision energy and thus particle refinement, yet excessive speeds can reduce collision effectiveness and introduce contamination. Similarly, while PCAs can suppress agglomeration by mitigating cold welding, they may also compromise powder yield and introduce secondary effects that limit scalability [11]. These knowledge gaps hinder the optimisation of mechanical alloying as a practical route for thermoelectric material development.

Therefore, the present study aims to systematically investigate the effects of milling speed and PCA addition on the structural, microstructural, and thermoelectric properties of Bi_2Te_3 synthesised by mechanical alloying. By correlating processing parameters with particle size evolution, microstructure, and performance indicators such as thermal conductivity and the figure of merit (ZT), this work seeks to clarify the balance between structural refinement, process efficiency, and functional performance. The findings are expected to provide new insights into scalable, cost-effective strategies for tailoring Bi_2Te_3 for thermoelectric applications.

2. MATERIALS AND METHODS

Mechanical alloying was performed at room temperature using a high-energy planetary ball mill (Model-P7, FRITSCH, GmbH, Germany). Commercial high-purity elements Bi_2Te_3 (Santech, China) were used as starting materials. The powder was kept in a zirconium oxide vial with zirconium oxide balls. The ball-to-powder mass ratio was 6: 1. Milling was paused after a selected time interval (5 min after every 10 min of milling). During the initial screening stage, five ball mill speeds have been examined: 200, 300, 500, 600, and 700 rpm, over a total duration of 10 minutes. 20 ml of ethanol, as process control agent, was added to the mill vial to study the effect of using PCA on the size reduction process.

The morphological and cross-sectional views of the nanocrystalline Bi_2Te_3 were observed by Field Emission Scanning Electron Microscopy (FESEM, Zeiss Merlin, Jena, Germany) operating at 10 kV−20 kV. The particle size of Bi_2Te_3 before and after the ball milling process was analysed using particle size analyser (PSA, Malvern Instruments, Zetasizer Nano ZS), where the particle size could be detected through the Zetasizer Nano software.

The electrical resistivity, ρ, and Seebeck coefficient, S, of the milled and unmilled Bi_2Te_3 were tested using the LSR-4/800 (Linseis, Bayern, Germany) under low pressure (10−2 torr). Rectangular bars cut from 12 mm pellets with dimensions of 11.5 mm × 2.4 mm × 2.4 mm were tested at numerous temperature points ranging from room temperature to 500 K.

3. RESULTS AND DISCUSSION

3.1 Particle Size Analysis

3.1.1 Effect of Milling Speed on Particle Size

Ball milling is a versatile solid-state processing method due to its ability to reduce material size (approaching nano-size) using simple equipment. This technique has become popular because of its simplicity, can be applied to all classes of materials, and can be used to produce materials on a large scale [12]. Analysis on the effect of ball mill speed on the size reduction process was conducted to identify the optimal ball mill speed to reduce the size of Bi_2Te_3. During the initial screening stage, five ball mill speeds were evaluated: 200, 300, 500, 600, and 700 rpm, over a total duration of 10 minutes.

The efficiency of the ball mill process is measured by PSA through D10, D50 and D90 [13] values as shown in Figure 1. The D90 parameter indicates the level of size distribution, where 90 % of the total volume of material in the sample is 'contained'. For example, if D90 is 844 nm, this means that 90 % of the sample has a size of 844 nm or smaller. Meanwhile, D50 is the size level where 50% of the material is contained. Similarly, D10 is the size where 10 % of the material is contained [14]. Based on Figure 1, a ball mill with a speed of 600 rpm produces the lowest D50 and D90 readings compared to other ball mill speeds. This observation shows that 600 rpm is the optimal ball mill speed to reduce the size of Bi_2Te_3.

The speed of the ball mill is closely correlated with the energy input to the Bi_2Te_3, but with certain constraints [8]. Generally, there is a maximum speed limit for ball mill operation. When this maximum limit is exceeded, the balls scatter to the sides of the ball mill vial, causing the collision between the balls and Bi_2Te_3 to be significantly reduced. This situation further hinders the size reduction process [15]. Furthermore, a higher ball mill speed can generate greater temperatures within the mill vial, potentially leading to material contamination.

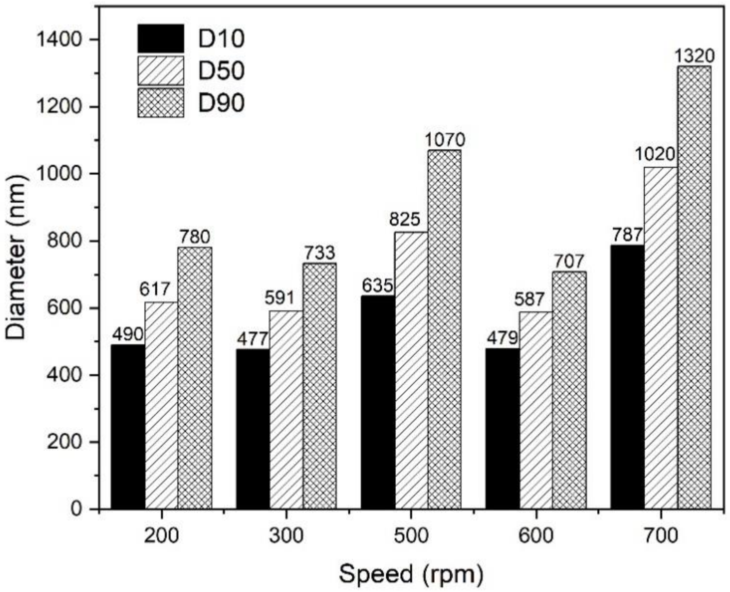


Figure 1: Effect of ball mill speed on average size of Bi_2Te_3

3.1.2 *Effect of process control agents on particle distribution and yield*

An analysis of the effect of using PCA on the size reduction process of Bi_2Te_3 was conducted to study the suitability of using PCA during the ball milling process. The PCA material, 20 ml of ethanol, was added to the mill vial. A ball mill with a speed of 600 rpm was employed, as indicated by the study conducted in Section 3.1.1. The particle size of Bi_2Te_3 was analysed using PSA. Table 1 lists the particle sizes of Bi_2Te_3 after the ball milling process was carried out using PCA and without PCA. Data from PSA shows that the lowest average size obtained through the ball milling process without PCA is 254 nm, while the lowest mode size produced through the ball milling process with PCA is 294.9 nm.

Table 1: Particle size using PCA and without PCA

Time (minute)	**With PCA**		**Without PCA**	
	Average size (nm)	**Mode size (nm)**	**Average size (nm)**	**Mode size (nm)**
10	584	294.9	2541	417.6

The efficiency of the ball milling process is measured by PSA through D10, D50 and D90 values. In comparison to the ball milling process without PCA, the use of PCA results in reduced D10, D50, and D90 readings, as shown in Figure 2. The use of PCA assists in the ball milling process by reducing the effects of cold welding. PCA is absorbed on the surface of the particles, minimising cold welding between particles, which indirectly reduces the effect of particle agglomeration [16].

However, from the experiments conducted, the powder yield from the ball milling process with PCA was low. Ethanol promoted finer particle dispersion but also limited recovery due to powder adhering to the vessel walls (sticking) and possible evaporation during milling. This trade-off between size control and yield efficiency has also been noted in other alloy systems where PCA selection strongly influenced process efficiency. Low powder yield indicates low efficiency of PCA. This low efficiency may be contributed by insufficient amount of PCA or an inappropriate selection of PCA [16]. Machio et al. [17] described a similar case in which using 2 % PCA resulted in less than 20 % powder yield. In this study, the PCA-assisted process was therefore excluded from subsequent optimisation to prioritise yield for bulk sample fabrication.

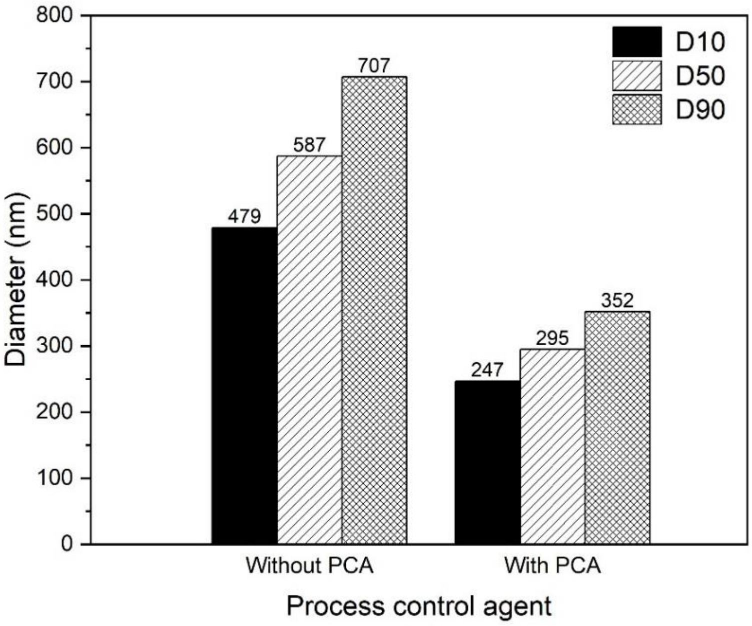


Figure 2: Effect of process control agents on the average size of Bi_2Te_3

3.2 Microstructural Characterisation by FESEM -EDX

The FESEM technique was employed to capture images of the microstructure of Bi_2Te_3 before and after the ball milling process, as displayed in Figure 3 and Figure 4. The ball milling process was carried out at a speed of 600 rpm without PCA base on the study conducted in Section 3.1.1. and Section 3.1.2. The ball mill operates with a 10-minute rotation time and stops for 5 minutes throughout the milling process to prevent heat generation during high-speed milling. In the extended milling process, the total milling time was set to be 260 minutes. Son et al. [18] reported that the size of Bi_2Te_3 particles decreased with milling time, but when the milling time exceeded 1800 minutes, Bi_2Te_3 particles were found to agglomerate with an average size exceeding 1 µm.

Figure 3 shows Bi_2Te_3 powder before going through the ball milling process. The starting powders consist of irregular fragments ranging from several microns down to submicron dimensions. Figure 4 shows Bi_2Te_3 powder after going through the ball milling process. After 260 minutes of intermittent milling at a speed of 600 rpm without PCA, the powders exhibited significant refinement, with particle sizes predominantly in the submicron range, though agglomeration of fine grains was evident.

These observations suggest that the milling mechanism involves an interplay of repeated fracturing and cold welding. While milling efficiently generates nanograins, the high surface activity promotes clustering, which limits complete dispersion. Such agglomerated structures are common in mechanically alloyed thermoelectric powders and often require post-processing treatments, such as controlled annealing, to improve homogeneity. EDX analysis shown by Figure 5 confirmed the stoichiometric retention of Bi_2Te_3 during milling, indicating that structural refinement was not accompanied by major compositional deviations.

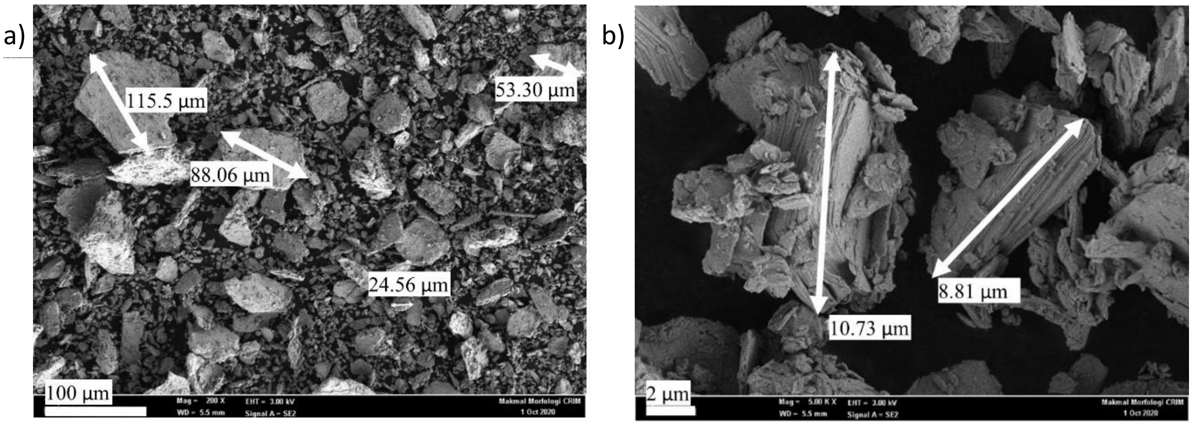
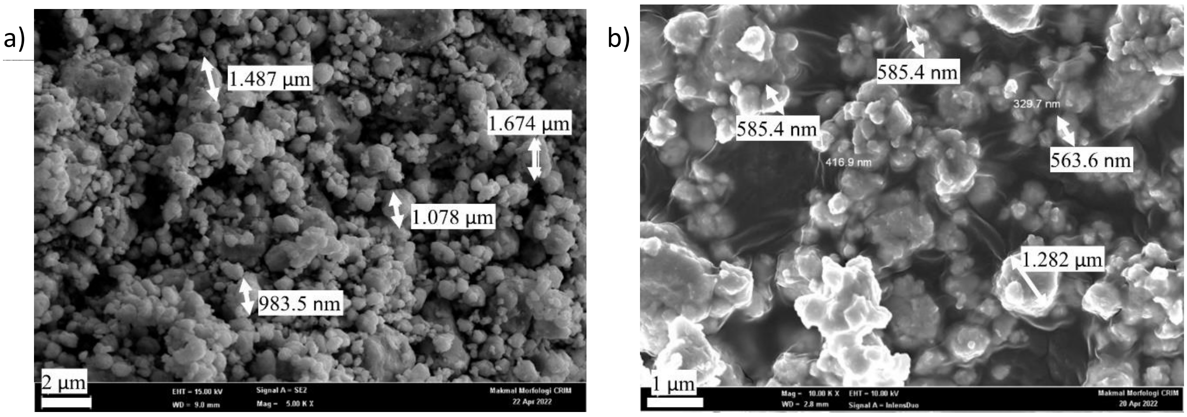
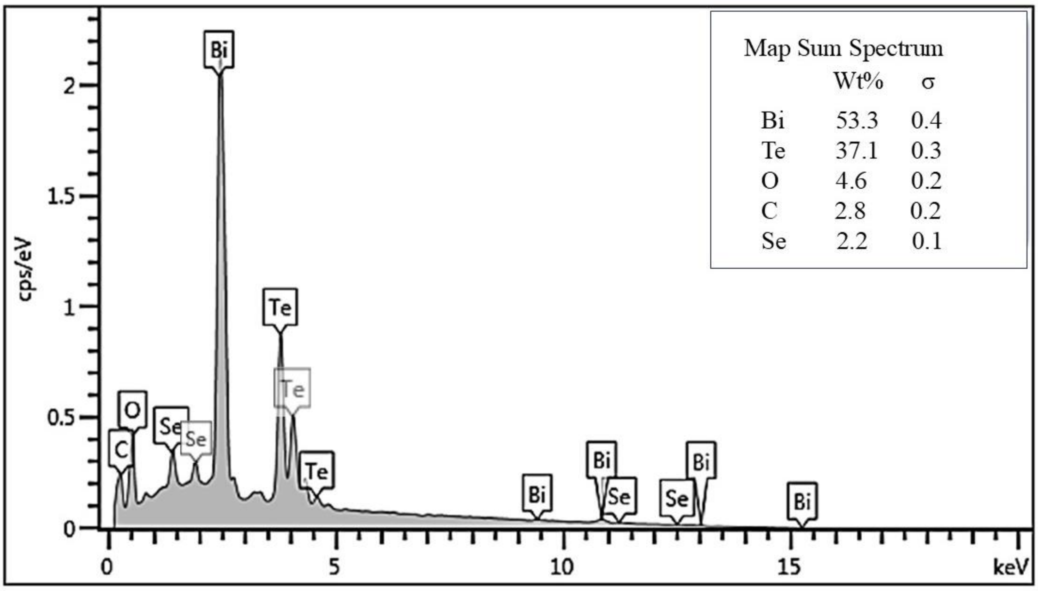


Figure 3: FESEM image of Bi_2Te_3 before ball milling process





Map Sum Spectrum

	Wt%	σ
Bi	53.3	0.4
Te	37.1	0.3
O	4.6	0.2
C	2.8	0.2
Se	2.2	0.1

Figure 5: EDX analysis of Bi_2Te_3 after ball milling process

Figure 4: FESEM image of Bi_2Te_3 after ball milling process

3.3 Thermoelectric performance

In this work, the performance of nanocrystalline Bi_2Te_3 synthesised by mechanical alloying to improve the TE properties of TE generators was studied. This study aims to deepen the understanding of how nanostructuring influences TE efficiency. TE generators' efficiency is determined by the material's performance, which is directly connected to the figure of merit, $ZT = S^2\sigma T/k$, where S, σ, k, and T denote the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively. Bi_2Te_3-based compounds have been widely commercialised as the best-performing room-temperature TE material.

The properties of milled and unmilled Bi_2Te_3 were compared to investigate the effects of nanocrystallinity on the performance of TE generators. The ball milling process was carried out at a speed of 600 rpm without PCA base on the study conducted in Sections 3.1.1. and 3.1.2. Carbon burial sintering was used to prepare the bulk milled and unmilled Bi_2Te_3 samples, as previously reported by Kristiantoro *et al.* [19]. Under pressure of 40 MPa, the sample was cold-pressed in a stainless-steel die with a diameter of 12 mm and a thickness of 2–3 mm. Then, the sample was put in the alumina crucible surrounded by carbon powders and sintered at 747 K for 6 h.

The temperature dependence of the thermal conductivity, k, for the milled and unmilled samples is shown in Figure 6(a). This result effectively demonstrates how nanostructuring decreases the k value of Bi_2Te_3, thereby improving its performance as a thermoelectric generator. Bi_2Te_3 in the 1 µm size range exhibits a lower k than Bi_2Te_3 in the 100 µm size range. This finding aligns with research reports by Pan *et al.* [20] that explain the reduction in k values in samples processed by ball milling compared to those without this process. The decrease in k values is attributed to reduced phonon scattering, which is a result of decreased grain size in the TE material. The difference in grain size of milled and unmilled Bi_2Te_3 used in this study is shown in Figure 3 and Figure 4. A smaller grain size results in a higher number of grain boundaries. Grain boundaries serve as obstacles that prevent phonons from moving freely. This enables the value of k to decrease as the grain size decreases. Figure 6(b) illustrates how the phonon scattering effect occurs as the number of grain boundaries increases.

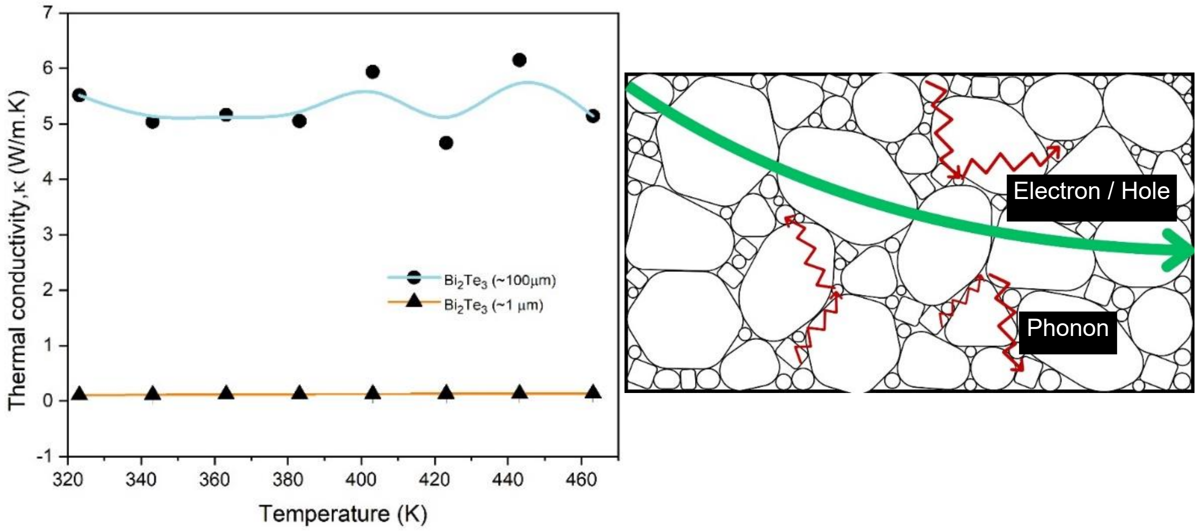


Figure 6: (a) Temperature dependence of thermal conductivity, k and (b) Phonon scattering effect mechanisms

The evaluated thermoelectric figure of merit, ZT of the milled and unmilled samples is shown in Figure 7. Electrical conductivity (σ) and the Seebeck coefficient (S) remained relatively stable in the milled samples, suggesting that carrier mobility was not significantly degraded by nanostructuring. As a result, the figure of merit (ZT) improved considerably in the milled sample. This finding supports the central hypothesis that mechanical alloying can reduce κ while preserving σ and S, leading to enhanced overall thermoelectric efficiency. Similar improvements have been reported in mechanically processed Bi_2Te_3 alloys, where grain boundary engineering was leveraged to suppress lattice thermal conductivity [20].

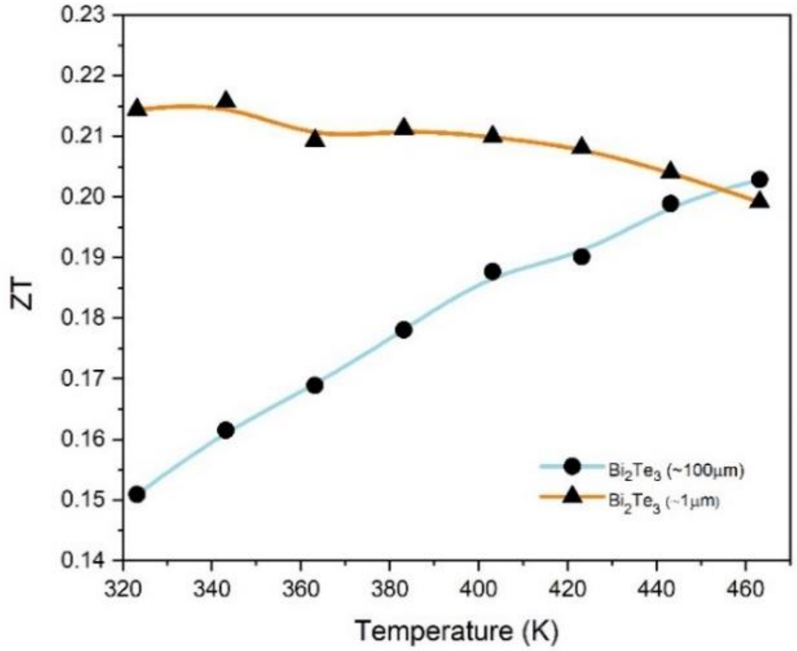


Figure 7: Temperature dependence of the ZT value of the milled and unmilled sample

4. CONCLUSIONS

This study demonstrates that mechanical alloying is a viable and scalable approach to synthesising nanocrystalline Bi_2Te_3 with improved thermoelectric performance. Systematic evaluation of milling speed revealed that 600 rpm provided the optimal conditions for grain refinement, while excessively high speeds reduced collision efficiency and hindered particle size reduction. The addition of ethanol as a PCA effectively suppressed agglomeration and promoted finer distributions, but at the cost of reduced powder yield, highlighting the trade-off between structural control and process scalability.

Microstructural characterisation confirmed the successful refinement of Bi_2Te_3 into the submicron range without significant compositional deviation, while thermoelectric testing established a clear reduction in thermal conductivity due to enhanced phonon scattering. Importantly, electrical transport properties were largely preserved, leading to a measurable increase in the figure of merit (ZT). These outcomes directly address the gap identified in the introduction, demonstrating that careful control of milling speed and PCA selection is critical for balancing microstructural refinement with process efficiency.

Overall, this work underscores the potential of optimised mechanical alloying to provide cost-effective and scalable nanostructuring routes for Bi_2Te_3, advancing its suitability for applications in waste heat recovery, cooling devices, and portable energy systems. Future work should extend this approach by evaluating alternative PCAs, longer milling durations, and scale-up to bulk modules to further validate the industrial feasibility of the process.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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