Field-assisted sintering of low-temperature thermoelectric material BiTeSe - sintering process and part characterisation

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Abstract. Field-Assisted Sintering Technology (FAST), an advanced consolidation technique, was employed to synthesise low-temperature thermoelectric n-type $Bi_2Te_{2.7}Se_{0.3}$ for energy harvesting applications. A systematic investigation of sintering parameters, including pressure, temperature, holding time, and heating rates, was conducted to optimise the material's properties. Post-sintering characterisation encompassed measurements of relative density, thermal conductivity, electrical resistivity, and Seebeck coefficient. Factor analysis revealed the hierarchical influence of sintering variables, with temperature emerging as the most critical parameter, followed by pressure and holding time. The study successfully identified optimal FAST sintering conditions for $Bi_2Te_{2.7}Se_{0.3}$, resulting in enhanced thermoelectric properties. This research demonstrates the efficacy of FAST in producing high-quality, low-temperature thermoelectric materials and provides valuable insights into the relationship between processing parameters and material performance.

1 Introduction

The global pursuit of sustainable energy solutions has intensified the focus on advanced materials for energy harvesting applications. Thermoelectric and piezoelectric ceramics have emerged as promising candidates due to their ability to convert thermal and mechanical energy into electricity, respectively [1, 2]. However, the widespread adoption of these materials has been hindered by challenges in achieving optimal material properties and cost-effective manufacturing processes. Field-Assisted Sintering Technology (FAST) has garnered significant attention as an innovative sintering technique capable of addressing these challenges [3, 4].

FAST sintering is characterised by the simultaneous application of uniaxial pressure and pulsed direct current (DC) through a conductive die containing the powder material [5]. This process generates Joule heating and potentially induces spark discharges between particles,

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although the exact mechanisms are still under debate [6]. The rapid heating rates (up to 1000°C/min) and the application of pressure (typically 20-100 MPa) facilitate densification at lower temperatures and shorter durations compared to conventional sintering methods [3].

The FAST process typically involves several key steps: (1) powder preparation and loading into a graphite die, (2) evacuation of the sintering chamber, (3) application of initial pressure, (4) rapid heating through pulsed DC current, (5) holding at the target temperature under pressure, and (6) controlled cooling [7]. The pulsed nature of the current is thought to contribute to the cleaning of particle surfaces and the formation of particle-to-particle necks, enhancing mass transport during sintering [8].

Recent advancements in FAST technology have led to the development of micro-FAST, a technique that enables the fabrication of miniaturised components with improved precision and performance [9]. Micro-FAST combines the principles of FAST with micro-forming techniques, allowing for the production of small-scale components with complex geometries and enhanced properties [10].

Building upon the foundational work of researchers like Yi Qin et al., who have demonstrated the potential of FAST for producing high-performance thermoelectric materials [11], this study extends the application of FAST to low-temperature thermoelectric ceramics BiTeSe. The comprehensive approach adopted in this research encompasses the entire process, from material synthesis to performance evaluation, providing valuable insights into the relationship between FAST processing parameters and the resulting material properties.

The material used in this research is n doped BiTeSe. Bismuth telluride selenide ($Bi_2Te_{2.7}Se_{0.3}$) is a ternary chalcogenide compound renowned for its superior low-temperature thermoelectric properties. This n-type semiconductor, characterised by its rhombohedral crystal structure, exhibits low thermal conductivity and high electrical conductivity in the 300K-500K range. The partial substitution of selenium for tellurium optimises the material's band structure and phonon scattering, enhancing its thermoelectric figure of merit (ZT) [12]. These attributes position BiTeSe as a prime candidate for low-temperature energy harvesting applications.

This study focuses on applying FAST sintering to the low-temperature thermoelectric ceramic powder $Bi_2Te_{2.7}Se_{0.3}$ for energy harvesting applications. Various sintering parameters, including pressure, temperature, holding time, and heating rates, were systematically varied to identify optimal conditions for this material. Post-sintering characterisation involved measuring relative density, thermal conductivity, electrical resistivity, and the Seebeck coefficient to evaluate the performance of the sintered parts. The results of this study have significant implications for the development of more efficient energy harvesting devices and contribute to the broader goal of sustainable energy production.

2 FAST sintering process for BiTeSe material

This section elucidates the Field-Assisted Sintering Technology (FAST) process utilised for low-temperature thermoelectric n-type $Bi_2Te_{2.7}Se_{0.3}$. The discussion commences with a comprehensive overview of the FAST sintering methodology employed in this investigation, encompassing a detailed description of the sintering apparatus and die configuration. Subsequently, the section examines the specific sintering parameters for each material, including applied pressure, sintering temperature, dwell time, and heating rates. Through a systematic analysis of these variables, the study aims to determine the optimal sintering conditions for this specific material, thereby establishing a foundation for subsequent characterisation and performance evaluation.

2.1 Overview of the FAST sintering technology

The Field-Assisted Sintering Technology (FAST) process in this study was conducted using a Gleeble 3500 thermomechanical simulator, located at the University of Swansea. The Gleeble 3500 is a versatile system adapted for FAST sintering applications, offering precise control over thermal and mechanical parameters critical for the sintering process. It features a direct resistance heating system capable of achieving heating rates up to 10,000 °C/s, which is crucial for maintaining fine grain structures and enhancing densification. The machine is equipped with a servo-hydraulic system that can apply static or dynamic forces up to 100 kN, essential for the pressure application during FAST sintering [13]. Figure 1 below shows the Gleeble system and vacuum chamber.

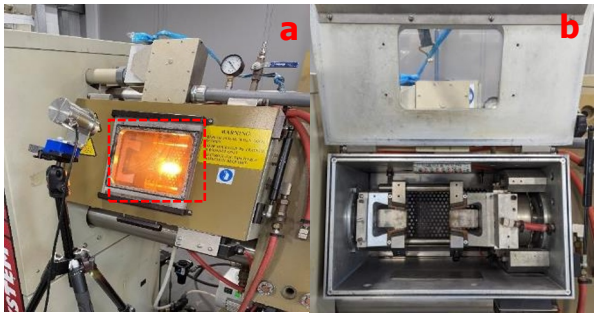


Fig. 1. Gleeble 3500 system and vacuum chamber used in this research

Temperature control in this research is achieved through a closed-loop thermal system using thermocouples embedded in the graphite die, coupled with a high-accuracy pyrometer, allowing for precise temperature measurement and control with accuracies within ±1°C. The system operates within a vacuum chamber that can achieve a vacuum level of 1×10^{-4} Torr/mmHg, preventing oxidation of the samples during sintering.

A custom-designed set of graphite dies was developed for compatibility with the Gleeble system. The assembly comprises a cylindrical sintering die and two complementary punches. A centrally located aperture in the sintering die accommodates thermocouple installation, enabling precise temperature monitoring. The specimen preparation procedure begins with the insertion of one punch into the die, followed by the incremental loading of pre-weighed ceramic powder. The powder undergoes cold compaction after each incremental addition to ensure uniform density. Upon completion of powder loading, both punches are inserted to encapsulate the specimen. The fully assembled die set is subsequently positioned within the vacuum chamber, secured by two tungsten carbide clamps to ensure proper electrical contact and force transmission. Figure 2 provides a schematic representation of the graphite die configuration.

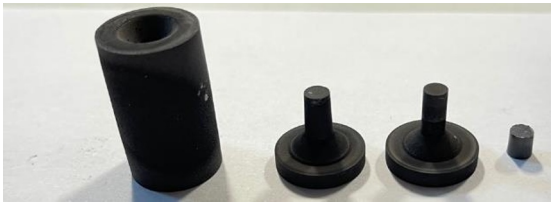


Fig. 2. Graphite die, punches and sintered part

Upon placement of the graphite die assembly within the vacuum chamber, the chamber is evacuated to achieve the desired low-pressure environment. Depending on the application, real-time monitoring of the sintering temperature is facilitated by either a K-type or R-type thermocouple. A pyrometer is positioned externally to the chamber to validate the temperature measurements, providing secondary temperature data. During the FAST sintering process, the graphite die set undergoes visible chromatic transitions, which

correspond to the variations in temperature. These colour changes serve as a visual indicator of the progression of the sintering process. Figure 3 provides a visual representation of the chromatic evolution of the die set throughout the FAST sintering procedure.

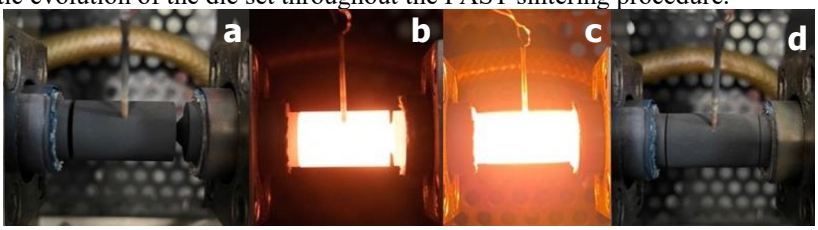
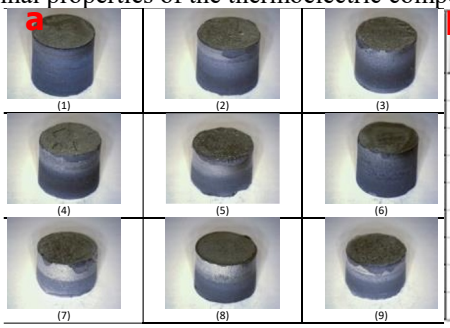


Fig. 3. Changes of die set during the FAST sintering process

Upon completion of the FAST sintering process, the die assembly is extracted from the vacuum chamber. Subsequently, the punches are carefully removed from the die to facilitate the retrieval of the sintered specimen. The cylindrical ceramic compact, illustrated on the right-hand side of Figure 2, represents the resultant sintered component. This specimen is then subjected to a comprehensive series of characterisation procedures to evaluate and validate its physical, thermal, and electrical properties. These post-sintering analyses are crucial for assessing the efficacy of the FAST process and determining the suitability of the sintered material for its intended energy-harvesting applications.

2.2 FAST-sintering of BiTeSe material

The low-temperature thermoelectric material, n-doped BiTeSe (chemical composition $Bi_2Te_{2.7}Se_{0.3}$), was synthesised using the FAST process. Figure 4(a) presents the visual characteristics of the sintered specimens, while Figure 4(b) delineates the specific sintering parameters employed for this material. These parameters encompass critical variables such as sintering temperature, pressure, heating rate and dwell time, which significantly influence the final properties of the thermoelectric compound.



b

Std	Factor 1 A:Temperature C	Factor 2 B:Heating rate K/min	Factor 3 C:Pressure MPa	Factor 4 D:Holding time min	Response 1 Density kg/mm3
1	700	40	10	15	6.905
2	700	50	15	10	6.811
3	700	60	20	5	7.017
4	800	40	15	5	6.952
5	800	50	20	15	7.169
6	800	60	10	10	6.972
7	900	40	20	10	7.312
8	900	50	10	5	7.061
9	900	60	15	15	7.411

Fig. 4. Sintered BiTeSe (a) and sintering parameters (b)

A factor analysis was conducted on the sintering parameters to ascertain their relative significance in the FAST sintering process. Table 1 presents a comprehensive breakdown of the contributions from various parameters.

Table 1. Factor analysis of sintering parameters

Factor	Standard variance	Degree of freedom	Variance	Contribution%
1(Temperature)	0.284	2	0.142	61.928
2(Heating rate)	0.033	2	0.016	6.753
3(Pressure)	0.079	2	0.040	16.980
4(holding time)	0.059	2	0.030	12.580
e(Error)	0.000	0		
Total (Sum)	0.455	8		

The results indicate that sintering temperature exerts the most substantial influence on the process, followed by sintering pressure and holding time. Notably, the heating rate demonstrates the least impact on the FAST sintering of BiTeSe material. The optimal sintering conditions for this material are 900 ℃ sintering temperature, 15 MPa sintering pressure, 60 ℃/min heating rate, and 15 minutes holding time. This hierarchical understanding of parameter influence facilitates the optimisation of the sintering process for enhanced thermoelectric performance.

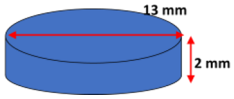
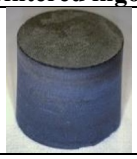
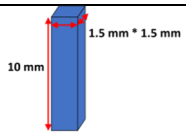
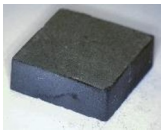
3 Characteristics of sintered BiTeSe

This section presents a comprehensive characterisation of the FAST-sintered $Bi_2Te_{2.7}Se_{0.3}$ samples. This analysis is crucial for evaluating the efficacy of the sintering process and determining the material's suitability for thermoelectric applications. The characterisation process is divided into four key subsections: sample preparation, density analysis, thermal properties, and electrical properties. Initially, the methodology for sample preparation is delineated. Subsequently, relative density measurements and X-ray diffraction (XRD) analysis are employed to assess the material's structural integrity and phase composition. Thermal conductivity measurements are then presented to evaluate the material's heat transfer characteristics. Finally, electrical resistivity and Seebeck coefficient measurements are analysed to determine the material's charge transport properties and thermoelectric performance. This multifaceted characterisation approach provides a comprehensive understanding of the relationship between FAST sintering parameters and the resultant material properties of $Bi_2Te_{2.7}Se_{0.3}$.

3.1 Sample preparation

The samples must be prepared according to the specifications to meet the requirements for thermal conductivity, electrical resistivity and Seebeck coefficient measurement. These include slicing, which cuts the sintered ingot into sizes slightly larger than the required size, then grinding them into the correct size, which also improves the surface finish. Table 2 below summarises the sample preparation process.

Table 2. Sample preparation for characteristics

Sample size	Sintered ingot	Slicing	Grinding
 Thermal conductivity sample			
 Electrical resistivity/Seebeck coefficient			

3.2 Relative density & XDR analysis

Relative density serves as a crucial indicator of the sintering process efficacy and material quality. It was calculated using the formula below.

$$relative\ density = \frac{measured\ density}{theoritical\ density} \times 100\% \quad (1)$$

The theoretical density of $Bi_2Te_{2.7}Se_{0.3}$ was estimated by calculating the weighted average of its constituent elemental densities. The molecular weight of the compound was determined to be 741.18 g/mol based on the atomic weights of bismuth (208.98 g/mol), tellurium (127.60 g/mol), and selenium (78.96 g/mol). The densities of these elements were sourced from the literature as 9.8, 6.24, and 4.81 g/cm³, respectively. So the estimated theoretical density is

$$\left(\frac{2\times208.95}{741.18}\times 9.8\right)+\left(\frac{2.7\times127.60}{741.18}\times 6.24\right)+\left(\frac{0.3\times78.96}{741.18}\times 4.81\right)=7.72\ \mathrm{g/cm^3}. \quad (2)$$

Higher relative density correlates with improved thermoelectric performance, attributed to enhanced charge carrier mobility and reduced phonon scattering at grain boundaries. Measured density was obtained using the Archimedes method, wherein samples were weighed in air and then immersed in liquid to determine their volume. As shown in Figure 5(a), sintered samples achieved relative densities up to 97.73%. X-ray diffraction (XRD) analysis, employed to assess phase purity and crystalline structure, revealed no discernible impurity phases, confirming the successful synthesis of single-phase $Bi_2Te_{2.7}Se_{0.3}$ via FAST sintering.

a

Std	Factor 1 A:Temperature C	Factor 2 B:Heating rate K/min	Factor 3 C:Pressure MPa	Factor 4 D:Holding time min	Response 1 Density kg/mm3	*Relative Density %
1	700	40	10	15	6.905	91.06%
2	700	50	15	10	6.811	89.82%
3	700	60	20	5	7.017	92.53%
4	800	40	15	5	6.952	91.68%
5	800	50	20	15	7.169	94.54%
6	800	60	10	10	6.972	91.94%
7	900	40	20	10	7.312	96.42%
8	900	50	10	5	7.061	93.11%
9	900	60	15	15	7.411	97.73%

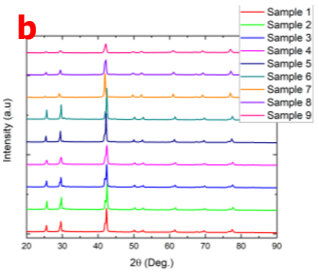


Fig. 5. Relative densities of sintered BiTeSe (a) and XDR analysis (b)

3.3 Thermal conductivity

Thermal conductivity is a crucial parameter in thermoelectric materials, influencing their efficiency in heat transfer and energy conversion. For thermoelectric materials, optimal thermal conductivity is essential for maintaining temperature gradients and enhancing performance. Conversely, lower thermal conductivity is preferred in certain thermoelectric applications to preserve temperature differences and improve the thermoelectric effect.

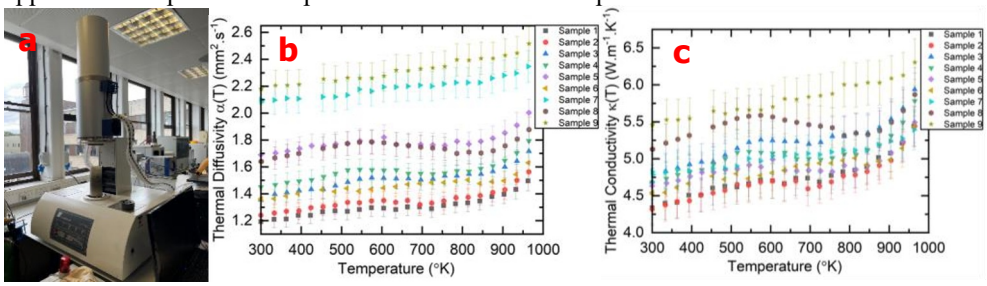


Fig. 6. Linseis system used in this study (a), measured thermal diffusivity (b) and calculated thermal conductivity (c)

In this research, the Linseis LFA 1000 system is utilised to measure thermal conductivity, as shown in figure 6 (a) above. The Linseis LFA 1000 employs the laser flash analysis (LFA) method, which involves subjecting a sample to a laser pulse and measuring the time it takes for the heat to traverse the sample. This technique is widely recognised for its accuracy and reliability in assessing the thermal conductivity of various materials. The method provides high precision, making it ideal for evaluating materials used in advanced energy applications.

The above-mentioned Linseis system can measure the thermal diffusivity (figure 6b) and convert the results into thermal conductivity using the following relationship.

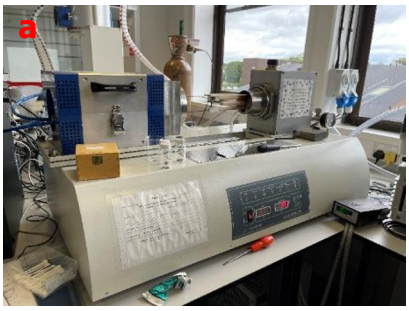
$$\alpha = \frac{k}{\rho c_p} \tag{3}$$

Where α is the measured thermal diffusivity, ρ is the measured density, c_p is the specific heat of the material, and k is the calculated thermal conductivity. Fig. 6 (b) and (c) illustrate the thermal behaviour of sintered $Bi_2Te_{2.7}Se_{0.3}$ across temperatures ranging from 300 K to 1000 K. The data reveal that samples with higher relative densities exhibit correspondingly higher thermal conductivity. This correlation underscores the importance of achieving high relative density in optimising the thermal properties of thermoelectric materials.

3.4 Electrical resistivity & Seebeck coefficient

Electrical resistivity and the Seebeck coefficient are critical parameters for thermoelectric materials, directly influencing their efficiency in energy conversion. Low electrical resistivity is essential for minimising energy losses and maximising electrical conductivity, which is vital for efficient thermoelectric performance. The Seebeck coefficient measures the voltage generated in response to a temperature gradient, and a high Seebeck coefficient indicates a material's strong thermoelectric potential.

The Linseis LSR-3 system shown in figure 7 (a) is employed to measure both electrical resistivity and the Seebeck coefficient. The system uses a four-point probe method for electrical resistivity, where a current is passed through the outer probes, and the voltage drop is measured across the inner probes. This setup ensures precise measurement by eliminating contact resistance.



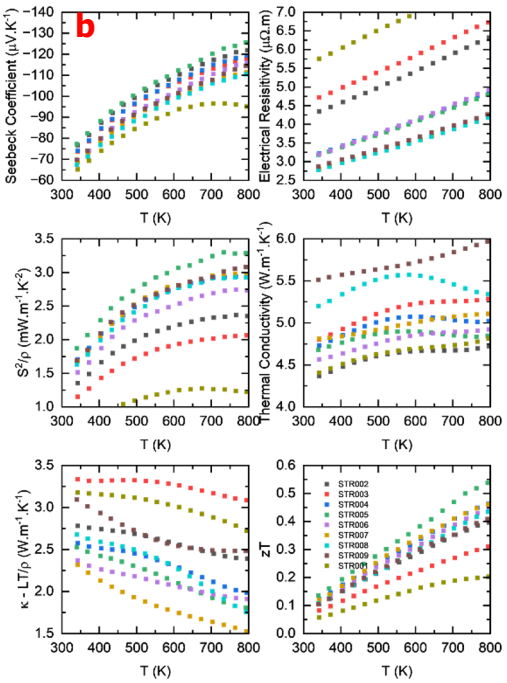


Fig. 7. Linseis system used in this study (a), measured Seebeck coefficient and electrical resistivity (b)

To measure the Seebeck coefficient, the LSR-3 system creates a temperature gradient across the sample and measures the resulting thermoelectric voltage. This method provides accurate and reliable data on the material's thermoelectric properties, which is essential for evaluating its suitability for energy harvesting applications.

The figure of merit for thermoelectric generators (TEGs), denoted as ZT, is a dimensionless quantity that measures the efficiency of a thermoelectric material in converting heat into electrical energy. It is defined as

$$ZT = \frac{S^2 \sigma T}{k} \tag{4}$$

Where S is the Seebeck coefficient, σ is electrical conductivity, k is thermal conductivity, and T is absolute temperature. Higher ZT values indicate improved thermoelectric efficiency. Figure 7(b) shows that samples with maximum relative density do not necessarily exhibit the highest ZT due to a corresponding increase in thermal conductivity.

Conclusion

In this study, the efficacy of Field-Assisted Sintering Technology (FAST) was demonstrated for sintering low-temperature thermoelectric material $Bi_2Te_{2.7}Se_{0.3}$. By systematically varying sintering parameters such as pressure, temperature, holding time, and heating rates, we identified the optimal FAST conditions crucial for achieving high density and superior material properties.

The characterisation of the sintered materials, including measurements of relative density, thermal conductivity, electrical resistivity, and the Seebeck coefficient, validated the effectiveness of the FAST process in enhancing the performance of thermoelectric ceramics. Overall, this research contributes to the understanding and application of FAST sintering technology, paving the way for the development of advanced materials with enhanced properties, essential for the next generation of energy harvesting systems. The findings underscore the versatility and effectiveness of FAST in producing high-quality thermoelectric ceramics, offering a promising approach for future material innovations.

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