REVIEW ARTICLE

A Review on Doped/Composite Bismuth Chalcogenide Compounds for Thermoelectric Device Applications: Various Synthesis Techniques and Challenges
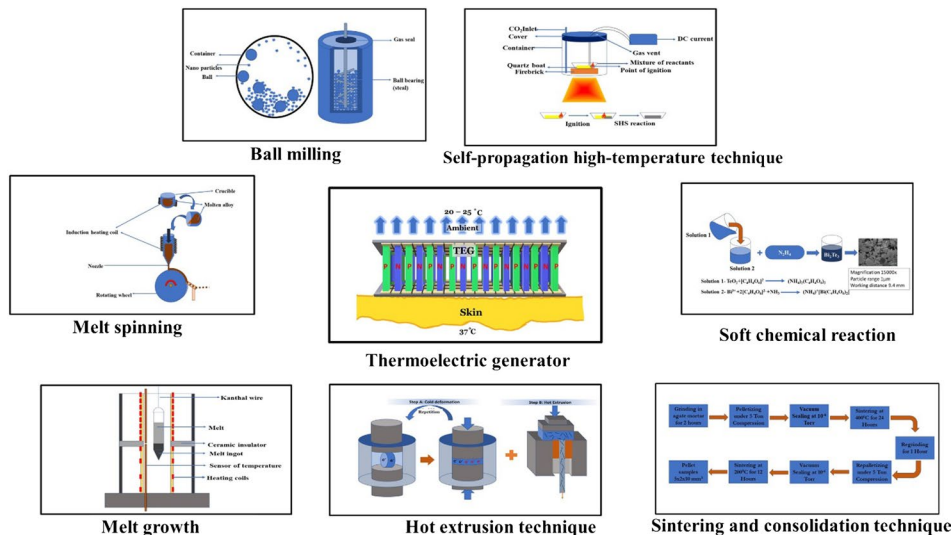
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Abstract

One of the global demands of primary research objectives is to achieve human energy harvesting and self-powered wearable technologies. Bismuth chalcogenides are the trending materials for thermoelectric generators and Peltier coolers due to their notable thermoelectric figure of merit in the low- and room-temperature range. Systematic alloying of bismuth chalcogenides leads to a substantial change in their electrical and thermal transport properties. The high thermoelectric figure of merit (ZT) observed in bismuth chalcogenides is due to the rhombohedral crystal structure, lower effective mass, low thermal conductivity, and large band degeneracy. This review is aimed at identifying and quantifying different techniques for effectively improving the thermoelectric properties of doped/composite bismuth chalcogenide compounds. The review also examines the various synthesis methods including ball milling (BM), spark plasma sintering (SPS), self-propagating high-temperature synthesis (SHS), soft chemical reaction, hydrothermal reaction, melt growth (MG), melt spinning (MS), sintering and consolidated synthesis, and hot extrusion, with their respective figures of merit. Since device modification is a challenging task, this report reviews the present research on bismuth chalcogenide alloys to benchmark future development using various techniques.

Graphical Abstract

Ball milling

Self-propagation high-temperature technique

Melt spinning

Thermoelectric generator

Soft chemical reaction

Melt growth

Hot extrusion technique

Sintering and consolidation technique

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Introduction

Thermoelectric materials have attracted global research interest due to their application in energy conversion from heat to electricity.[1] Thermoelectric technology is effectively applied in commercial thermoelectric coolers and stabilizers.[2,3] During the last two decades, attention has been given to thermoelectric technology, mostly due to the increased demand for energy harvesting through waste heat. Thermoelectric materials are assessed by the dimensionless quantity called the figure of merit $ZT = \frac{S^2\sigma}{K}T$ where S is the Seebeck coefficient, K is the thermal conductivity, σ is the electrical conductivity, and T is the applied temperature. Researchers have been working over the past five decades to increase the thermoelectric figure of merit. Recently, Joseph et al. and Zhang et al. succeeded in improving the ZT value above unity.[4,5] There are a few compounds that have a high thermoelectric figure of merit, such as skutterudites,[6,7] half-Heuslers,[8,9] clathrates,[10,11] selenides,[12–16] and lead-based compounds.[17–19] It has been observed that material processing plays an essential role in enhancing the thermoelectric figure of merit.

Bismuth telluride and bismuth selenides are found to be functional thermoelectric materials for low- and near-room-temperature applications because of their low thermal conductivity and high weighted mobility. The performance of these materials is also influenced by the minority carriers.[20] Alloys of $Sb_2Te_3/In_2Te_3/In_2Se_3$ decrease the bipolar effect by increasing the band gap. Both electrons and holes are excited by filling the conduction band and valence bands close to the Fermi level for a particular bandgap. This implies that more heat is absorbed near the hot end and more heat is released near the cold end because of electron–hole recombination, resulting in high thermal conductivity, which negatively impacts the ZT and the power factor.[21] In addition, the transport properties of bismuth chalcogenides need to be considered.[22–25] High-frequency phonon scattering is significantly responsible for lowering thermal conductivity by introducing mass contrast and bonding variations.[26,27] The presence of density barriers in the material creates selective charge scattering and causes charge mobility variation. In this situation, a few mobility charges are suppressed, and they move to the onset of mixed conduction, resulting in the enhancement of ZT values.[28] These details must be considered when introducing any foreign elements/composite into the matrix of Bi_2Te_3 and Bi_2Se_3.[29] The valence band structure for binary compounds of chalcogenides bismuth selenide and telluride is similar except for the differences in their valence band maxima.[30] In chalcogenides, there is a crossing over of band edges in order to increase thermopower.

The thermoelectric properties of chalcogenides can also be engineered by tuning the microstructure and surface morphological features. Since Bi_2Se_3/Te_3 is bonded with van der Waals forces between layers, there is a need for substitution on Bi sites by suitable dopants like In/Sb/Sn/Ge, which leads to two quintuple layers of Bi_2Te_3/Se_3 and $InTe/Sb_2Te_3/GeTe/SnTe$.[31] The insertion of In/Sn/Sb yields an extra electron to the Bi_2Se_3/Te_3 lattice, in which an enhancement in the carrier concentration is noticeable.[32,33] The impact of dopants leads to a narrow peak in the electronic density of states, at the top of the valence band or at the bottom of the conduction band. The dopants also act as an acceptor or donor impurity and pin the Fermi level to the conduction band by creating the delocalized charge carriers which resonate between the band and impurity states.[34] It is observed that phonon scattering is dominant at low carrier concentrations and low temperatures, which reduces thermal conductivity. However, at higher doping concentrations (alloying), the phonon scattering rates increase by point defects, contributing substantially to the reduction in thermal conductivity, except for phonons with fewer frequencies.[35] The replacement of In/Sb/Sn on Bi promotes the formation of antisite defects of Bi_2Se_3/Te_3.[36–38] The challenging task is to reduce thermal conductivity without weakening the electrical conductivity, which inspires us to review different methods and processing techniques for the synthesis of bismuth chalcogenides.

The embedded thermoelectric generator (TEG) can be optimized on the device and system levels to safeguard the working of a heat harvesting system. Human skin is a multilayer structure containing fat, dermis, and epidermis. Heat interchange occurs through the skin surface due to convection, radiation, evaporation, and blood perfusion. The thermal resistance of the skin is highly reliant on the contact pressure, and skin features such as the surface of human skin are soft but intrinsically rough. Hence the effect of thermal contact resistance at the interface of the skin and TEG on the performance of the wearable thermoelectric device is very significant.[39,40] The materials should have high thermopower for the efficient operation of a boost converter.[41] The surrounding air velocity and ambient temperature affect the power produced by the TEG. The temperature of the core part of the body is usually independent of ambient temperature due to the physiological thermoregulatory system. Hence, the skin's surface temperature is considered the ambient temperature and does not significantly change the environment.[42] With an increase in ambient temperature, the temperature gradient of the TEG decreases, whereas in a warm climate, the ambient temperature rises more than the surface body temperature by the production of power. When the temperature gradient is precisely equal to the skin temperature, the TEG does not generate any temperature difference between the two junctions, with the saturation of rejected heat in an extremely high-velocity air condition.[42,43] The performance of the wearable TEG is affected

by the free air velocity cooling on the cold side. Usually, skin temperature of 28°C to 33°C is applied to the bottom of the metal sheet, while the ambient temperature remains at 23°C. Natural air convection is used on the top of the heat sink. Then, the TEG has the highest temperature gradient and power due to the skin contact. The body gradually heats the TEG and the heat sink until the system reaches a steady state.[44] It is worth knowing that other environmental effects such as humidity and air pressure can also affect the TEG performance. If a TEG has a minimal number of legs, the energy conversion is low because the load resistance is insufficient to obtain a sufficiently high voltage. Inversely, if a TEG has a more significant number of legs, the complete equivalent resistance of the TEG increases, and relatively high Joule losses occur in the TEG. Besides, thermopower is directly proportional to the output voltage. This condition is very important for increasing energy conversion. Hence, the voltage output cannot be improved by having a more significant number of TE elements even if the material's thermopower is small.[45]

So far, many processes have been employed to prepare thermoelectric compounds. Therefore, a timely review is needed of the different methods and their effect on thermoelectric materials. Few review articles are available summarizing the present status of the research on thermoelectric materials.[46] Hence, in this review article, the emerging techniques with description of the working principles are reviewed, and an attempt is made to link the methods, microstructure, and respective thermoelectric properties of doped/composite bismuth chalcogenides. The aspect of the physiology of the human body involved in the production of heat is elaborated. The effects of various parameters on the function of TEGs are reviewed at the material, device, and system levels.

Electronic Structure

Bismuth telluride is an excellent thermoelectric material due to its complex electronic structure, and it has been widely investigated both theoretically and experimentally. The simple valence rules and spin–orbit interactions complicate the band structure, providing exceptional thermoelectric performance for the material. The qualitative performance of Bi_2Te_3 is governed by the p-states of valence interactions within a quintuple layer. $Te^{(1)}$ atomic layers between non-bonding adjacent quintuple layers donate to the top of the valence band through van der Waals interactions. Unfilled anti-bonding p-states of bismuth are bonded with tellurium. Two anti-bonding and two bonding sites between Bi and Te atoms of polar bonding are the reason for the positively charged behavior of bismuth. The band structure connects the valence and conduction bands to form a Dirac cone at the surface. The applied electric field produces the spin-polarized current. By monitoring the Fermi level, the magnitude and spin polarization of the current magnitude and direction can be controlled.[47]

In some cases, bismuth telluride is considered a cubic structure that is viewed along the (111) axis. This can be visualized by linking the atoms to their closest neighbors in the planes below and above in units of five plane values which are near 90° within a few degrees in bismuth.[48] Based on the molecular orbital structure, there is an interaction between $Te^{(1)}$–$Te^{(1)}$. It is observed that the band gap has no contribution on $Te^{(2)}$, which deals with the difference in the shape of the lower p orbital in $Te^{(1)}$ and $Te^{(2)}$ with limited densities of states in the fitted binding model. Covalent bonding is preferred between Te and Bi using a full tight-binding model. A schematic diagram of the electronic band structure is shown in Fig. 1.[49]

Bismuth telluride and bismuth selenide have drawn attention as a practical material in applications such as conventional thermoelectric systems. The Bi_2Te_3/Se_3 crystal structure is a rhombohedral tetradymite type with space group $R\bar{3}m$ and is defined by a hexagonal unit cell, as shown in Fig. 2a and b. The Te/Se unit cell comprises five covalently bonded monatomic sheets along the c-axis in the sequence $-Te/Se_{(1)}-Bi-Te/Se_{(2)}-Bi-Te/Se_{(1)}-Bi-Te/Se_{(2)}-Bi-Te_{(2)}/Se_{(2)}-Bi-Te_{(1)}/Se_{(1)}$. Due to this crystal structure, the lattice constant of the c-axis is approximately seven times as large as that of the a and b axes, leading to remarkable anisotropic behavior.

In bismuth-, tellurium-, antimony-, and indium-doped alloys, negatively charged antisite defects such as Sb_{Te}, Bi_{Te} and In_{Te} are created when there is excess cation occupancy on empty anion sites, which prefer p-type conductivity between compounds.[50,51] Anion vacancies $V_{Te}^{\cdot\cdot}$ and $V_{Se}^{\cdot\cdot}$ accompanying positive charges are produced when the vacant anion sites are retained and are satisfied by the electrons. The antisite defect concentration of solid solutions is dependent on composition and doping, where more minor differences in atomic radii and electronegativity are present between cations and anions.[52]

Various Synthesis Techniques

The synthesis process has a vital role in obtaining the desired thermoelectric materials (TEM). The past two decades have witnessed the emergence of different techniques for preparing thermoelectric compounds. Cost-effective and straightforward strategies such as solid-state reaction and melting still play a vital role in producing high-performance TEMs. In addition, there are a few progressive preparation techniques including high-energy ball milling and mechanical alloying to obtain TEMs
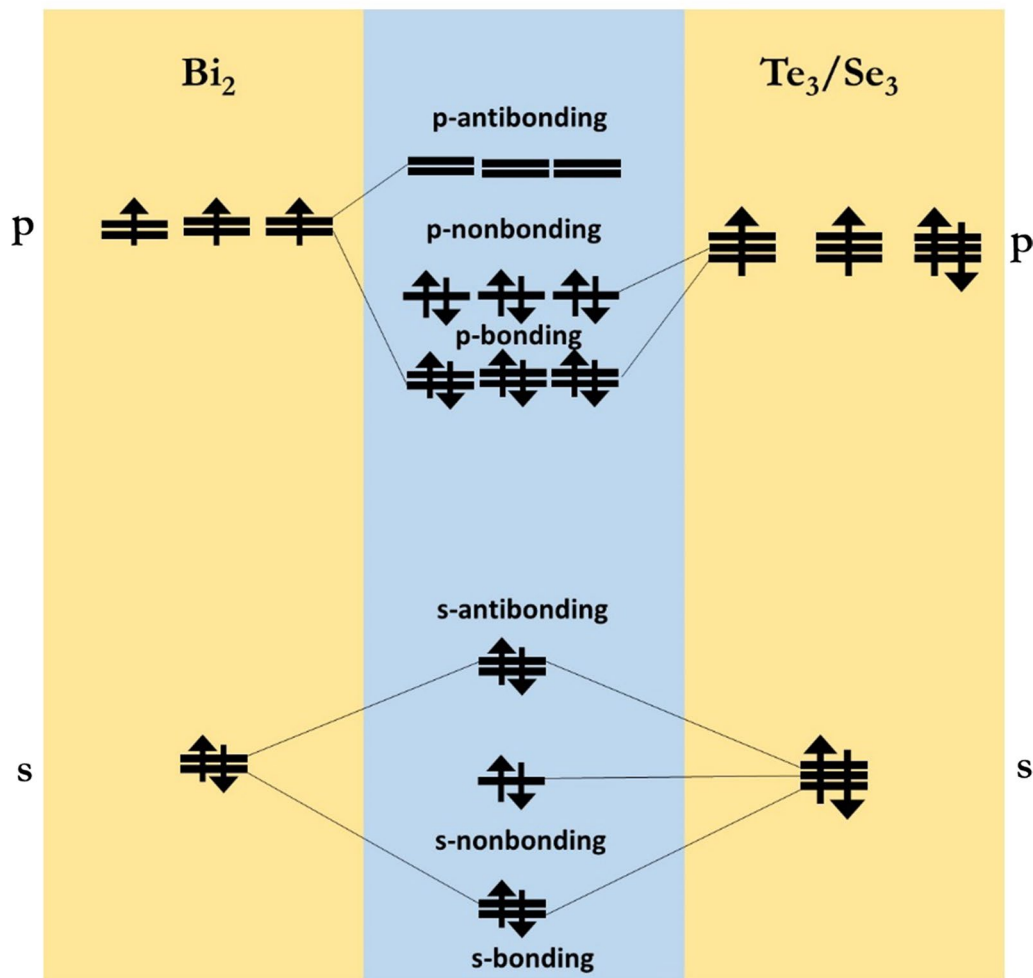
Fig. 1 Energy level diagram of Bi_2Te_3/Se_3.

in powder in bulk form.[53] Chemical synthesis methods like hydrothermal and solvothermal techniques are used around the globe to control the morphology, dimensions, and size of the materials.[54] Synthesis by grinding and sintering plays an active role in preparing bulk TEM. In melting and casting methods, the compounds are deliberately crushed and sintered again to regulate the grain size, particle size, lattice parameters, and strain.[55] For layered compounds like Bi_2Te_3, Bi_2Se_3, InTe, InSe, etc., melting/zone melting techniques are utilized because these techniques are useful in purifying the phase of the compounds.[56]

In the present section, we mainly emphasize the emerging methods of producing nanostructure/polycrystalline TEMs and their operating principles with respect to their structural, morphological, and thermoelectric properties.

Ball Milling (BM)

Ball milling is one of the most widely used pulverizing techniques and can be applied as mechanical alloying (MA) and mechanical grinding (MG). MA can be used to synthesize compounds from elemental powders by a mechanochemical effect.[57,58] The collision energy between the balls is successfully relocated to milled powders to conduct the reaction in a dry milling form.[59] Mixing mills, planetary ball mills, and shakers are the various BM machines, although the operating principles for each instrument are similar. The main purpose of using BM is to synthesize the compounds to obtain micro-grains or nanostructured powders and to combine composites.[60,61] The ratio of large balls to small balls, BM speed, time, and number of balls can be adjusted to obtain the optimized intensity of pulverizing. In addition,

fracturing and cold welding in high-energy ball mills leads to further grinding.[62] Excessive cold welding is resisted by steric acid when ductile powders are crushed. The refined structure increases the scattering of phonons in order to decrease thermal conductivity. Using BM combined with a subsequent hot-press technique, Poudel et al. obtained a *ZT* value of 1.4 at 400 K for BiSbTe nanocrystals. The bipolar effect was reduced by the existence of an interfacial potential that scattered more electrons than holes.[63]

On the other hand, BM also exhibits a remarkable effect on the electrical transport properties of compounds due to the impedance of carrier transport in nanostructures.[64]

Charge density is exaggerated when charge point defects are introduced into alloys based on chalcogenides such as bismuth telluride and bismuth selenide and using Sb, In, Sn dopants.[65–67] Bi_2Te_3 is usually a p-type material because of antisite defects which are negatively charged, and it changes to an n-type material due to a higher number of donor-like effects and anion vacancies.[65–69] A comparison of the thermoelectric performance of ingots and bulks of spark plasma sintered (SPS) pellets (BM + SPS) of n-type BiTeSe and p-type BiSbTe was reported by Hue et al.[70] As noted by Liu et al.,[71] the free charge density of BiTeSe has five times more scattering than p-type BiSbTe with the evaporation of
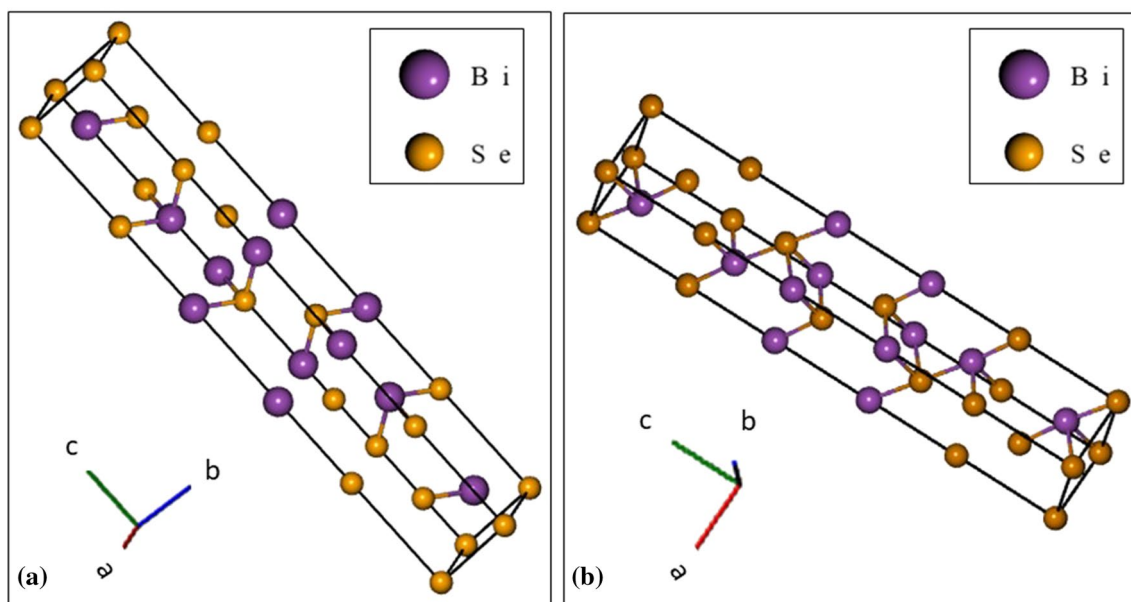
Fig. 2 (a) Schematic diagram of Bi_2Se_3 crystal structure (CIF id: mp-342022). (b) Schematic diagram of Bi_2Te_3 crystal structure (CIF id: mp-541837) (images generated by the software BURAI Quantum ESPRESSO).
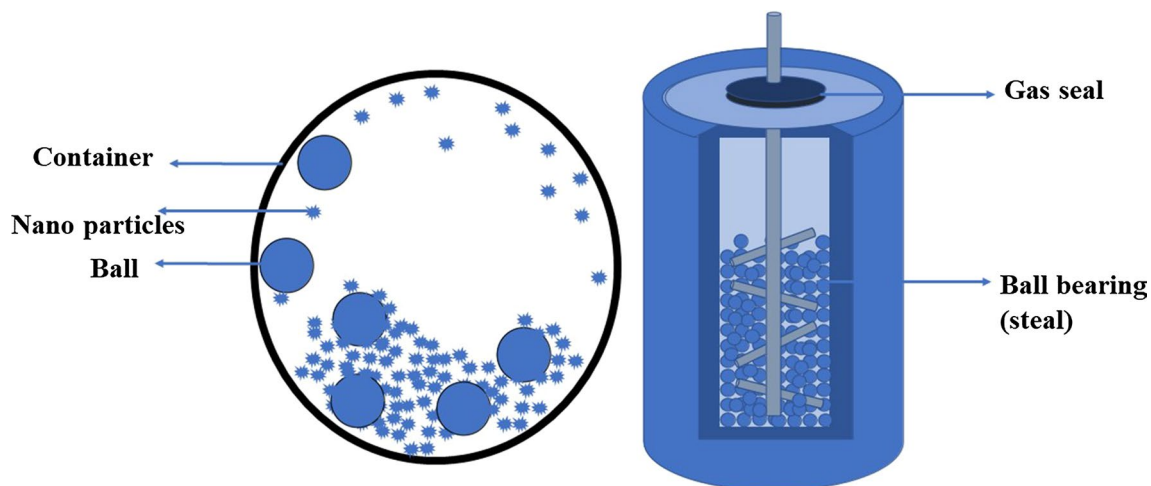
Fig. 3 Schematic of ball milling bismuth chalcogenide.

Te ions. A schematic diagram of ball milling is shown in Fig. 3. BiTeSe has much less reproducibility under the BM process.[72,73] Some of BM-synthesized materials are reported in Table I.

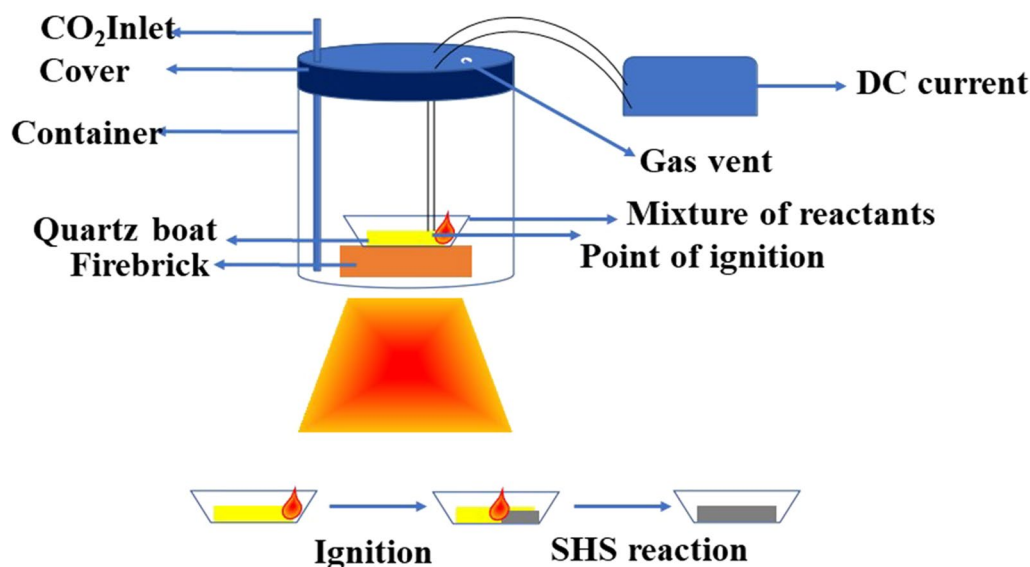## Self-Propagating High-Temperature Synthesis (SHS)

Self-propagating high-temperature synthesis is an analogous auto wave procedure for the propagation of combustion movement introduced by point heating a sample's minor portion.[74,75] The chemical reaction is contained in the combustion region, which impulsively proliferates on a chemical dynamic medium. The materials are purified by maintaining the stoichiometric ratio as the combustion wave permits over the sample.[76,77] The current procedure can be adapted mainly for inorganic materials such as bismuth, indium, tellurium, and selenium.[78–80]

SHS synthesis offers advantages including a one-step process, scalable nature, and maintenance of stoichiometry, making some of the thermoelectric materials very popular.[74,81] In the SHS process between binary reactants, the combustion reaction continues in the mode of diffusion, and the reaction rate is partly through the second reactant diffusion. The nano-sized products are obtained from nanoscopic reactants, providing in situ nanostructures in the resultant thermoelectric materials.[75] These nano-sized materials are influenced by mechanical action. As there is an increase in reactant reactivity, there is a corresponding increase in defect concentration which significantly induces automatic activation of reactants; however, the controlled propagation process wave is a vital task.[82] A

Table I ZT values of some reported bismuth chalcogenide-based compounds prepared by various synthesis techniques

Sl. no.	Compound	Technique	Thermoelectric figure of merit (ZT)	Temperature (K)
1	Bi_2Te_3+SiC	Ball milling	0.65	450[108]
2	$Bi_2Te_{3-x}Se_x$	Ball milling	1.29	398[109]
3	Bi_2Te_3	Ball milling	1.0	300[60]
4	$(Bi,Sb)_2Te_3$	Ball milling	1.0	323[110]
5	$Bi_2Te_{3-x}Se_x$	SHS	0.94	420[77]
6	Bi_2Te_3	SHS	0.39	300[111]
7	$Bi_2Se_{1.5}Te_{1.5}$	SHS	0.70	500[112]
8	Bi_2Te_3	SHS	0.65	450[113]
9	Bi-Sb-Te	Soft chemical reaction	1.28	303[114]
10	Bi_2Te_3	Soft chemical reaction	0.70	473[97]
11	$Bi_{0.5}Sb_{1.5}Te_3+ Sb_2Te_3$	Soft chemical reaction	0.55	400[115]
12	Bi_2Te_3	Soft chemical reaction	0.54	400[116]
13	$Bi_2Te_{3-x}Se_x$	Soft chemical reaction	0.57	475[117]
14	$(Bi_{0.2}Sb_{0.8})_2Te_3$	Melt spinning	0.55	300[118]
15	$Bi_2Te_{2.4}Se_{0.6}$	Melt spinning	1.05	300[119]
16	$Bi_2Te_{2.7}Se_{0.3}$	Melt spinning	0.84	423[120]
17	$Bi_{0.52}Sb_{1.48}Te_3$	Melt spinning	1.56	300[121]
18	$Bi_2(Te,Se)_3$	Melt spinning	1.05	420[122]
19	$Bi_{1.5}Sb_{0.5}Te_{2.7}Se_{0.3}$	Melt growth	1.05	330[123]
20	$Bi_2Te_3-Sb_2Te_3$	Melt growth	0.03	300[124]
21	$Bi_{1.85}In_{0.5}Te_2Se_1$	Melt growth	1.1	300[67]
22	$Bi_{0.5}Sb_{1.5}Te_{3-x}Se_x$	Melt growth	1.1	300[125]
23	$(Bi_{0.98}In_{0.02})_2Se_{2.7}Te_{0.3}$	Melt growth	0.28	350[126]
24	$(Bi_{0.96}Sn_{0.04})_2Se_{2.7}Te_{0.3}$	Solid-state reaction and sintering	0.27	300[127]
25	Bi_2Te_3	Sintering	1.6	420[128]
26	$Bi_{2-x}Sb_xTe$	Sintering	1.2	360[129]
27	$(Bi_{0.98}In_{0.02})_2Te_{2.7}Se_{0.3}$	Solid-state reaction and sintering	0.67	350[50]
28	$(Bi_{0.98}In_{0.02})_2Te_{2.7}Se_{0.3}$	Solid-state reaction sintering	0.023	350[51]
29	$Bi_2Te_{2.7}Se_{0.3}$	Hot extrusion	0.9	300[130]
30	$Bi_2Te_{2.7}Se_{0.3}$	Hot extrusion	0.9	300[131]
31	$Bi_2Te_{2.7}Se_{0.3}+SbI_3$	Hot extrusion	0.96	300[132]

Fig. 4 Basic schematic representation of self-propagating high-temperature technique.

schematic representation of the SHS technique is provided in Fig. 4.

Soft Chemical Reaction (Wet Chemical Process)

In some nanostructured thermoelectric compounds, the controlled surface morphology is achieved by wet chemical processes, including the sol–gel technique, solvothermal synthesis, and microwave synthesis. The pros and cons of the solution-based synthesis process are discussed in this section. The precursor of ingredients is combined in superior templates in a stoichiometric ratio of an aqueous solution. The solution is inserted into a closed autoclave with chosen heating temperature followed by cooling to room temperature. The autoclave strictly controls the pH value, pressure, and additive concentration. It is noted that the morphology and grain size can be altered through the peripheral condition. Zhao et al.[83] reported Bi_2Te_3 nanotubes having diameters less than 100 nm by performing hydrothermal synthesis. Many reports are available on this technique, in which $BiCl_3$ and TeO_2 are used as initial precursors.[84–89] To reduce toxicity, Muramatsu et al.[90] applied green hydrothermal solution synthesis using ascorbic acid in an aqueous solution as a reducing agent.

Microwave synthesis (MWS) has been used consistently for the large-scale one-pot preparation of thermoelectric materials.[91–93] Although solvothermal synthesis was established with regulation over the surface morphology and size of the particle, it has been observed that sintering is a fairly difficult task because of low density and an increase in the secondary phase of compounds. Industrialization of the MWS method was performed by Li et al.[94] for a SnTe

compound by varying the sizes from micro- to nanoscale using a period of 20 min, which enhanced the *ZT* by 2.3 times over that of the powder synthesis method. However, there are some unavoidable experimental constraints for the MWS method: (i) requirement of practical experiments on applicable parameters; (ii) superheating, speculation of hotspots, and the hot surface of nonthermal effect caused due to the extreme measurement of reaction pressure and temperature; and (iii) some of the complex system synthesis was found to be a tough task in the MWS technique for developing and designing thermoelectric nanostructures.[95,96] Some of the available thermoelectric materials prepared by solvothermal method are mentioned in Table I. Figure 5 shows a schematic representation of soft chemical reaction synthesis technique.

Melt Spinning (MS)

Melt spinning is a beneficial technique for quick molten solution cooling. A molten alloy thin stream is poured on a spinning wheel.[97–99] The melting heat is quickly transferred to the wheel followed by rotation, which sustains the amorphization of liquid continuously, producing thin tapes and ribbons.[100] The local cooling and cooling rate regulate the microstructure of the materials in the synthesis process and are maintained through processing parameters in melt spinning.[101] Lee et al. showed that ribbons can be made thin monotonically by increasing the wheel's speed and cooling rate. Si-Ge-Au showed a *ZT* of 2 at 300 K when prepared by the MS method.[89] Dey et al.[102] observed a *ZT* of 0.14 for BiSbTe at 350 K. The unique nanostructure and microstructure produced in the melt spinning process

led to enhanced thermoelectric performance. Low-dimensional structures of an amorphous nature with 5–15-nm nano-crystallites with coherent interfaces were observed. These interfaces were supposed to be the center of strong phonon scattering zones, which deliver the route for conduction of charges, which is beneficial for thermoelectric performance.[103] A schematic diagram of melt spinning is represented in Fig. 6. Thermoelectric figure of merit values of some reported materials are given in Table I.

Melt Growth (MG)

One of the rich conventional methods for preparing single-crystal thermoelectric materials is the melt growth (MG) technique. Melting is a unidirectional solidification procedure applied for materials like Bi_2Te_3, Bi_2Se_3 in industries.[104] In laboratories, chalcogenide compounds are taken in a quartz tube sealed in a vacuum of 1.333×10^{-7} kPa, and the temperature profile is prearranged in a crystal puller. With the help of a programmed thermal profile,

Solution 1- $TeO_2 + [C_4H_4O_6]^2 \longrightarrow (NH_4)_2(C_4H_4O_6)_2$

Solution 2- $Bi^{3+} + 2[C_4H_4O_6]^{2-} + NH_3 \longrightarrow (NH_4)^+[Bi(C_4H_4O_6)_2]$

Magnification 15000x
Particle range 1μm
Working distance 9.4 mm
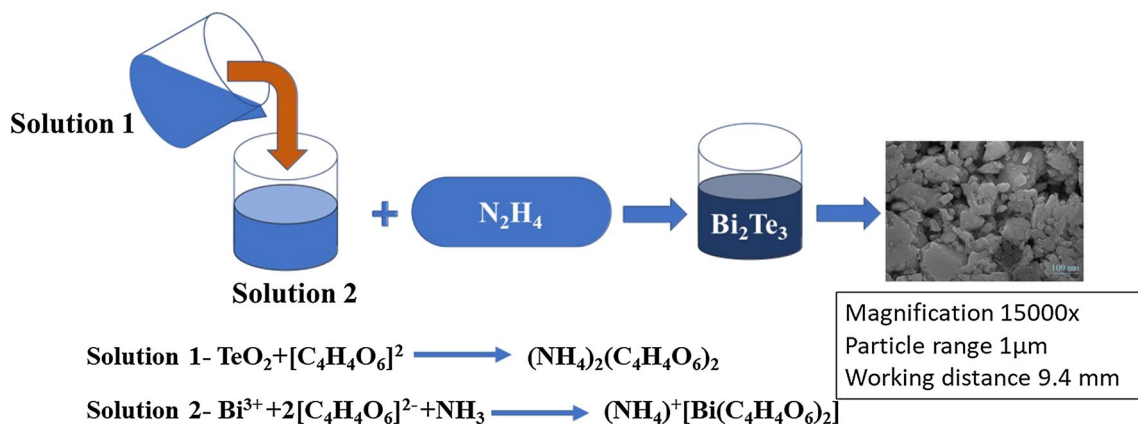
Fig. 5 Schematic representation of soft chemical reaction of bismuth telluride synthesis.
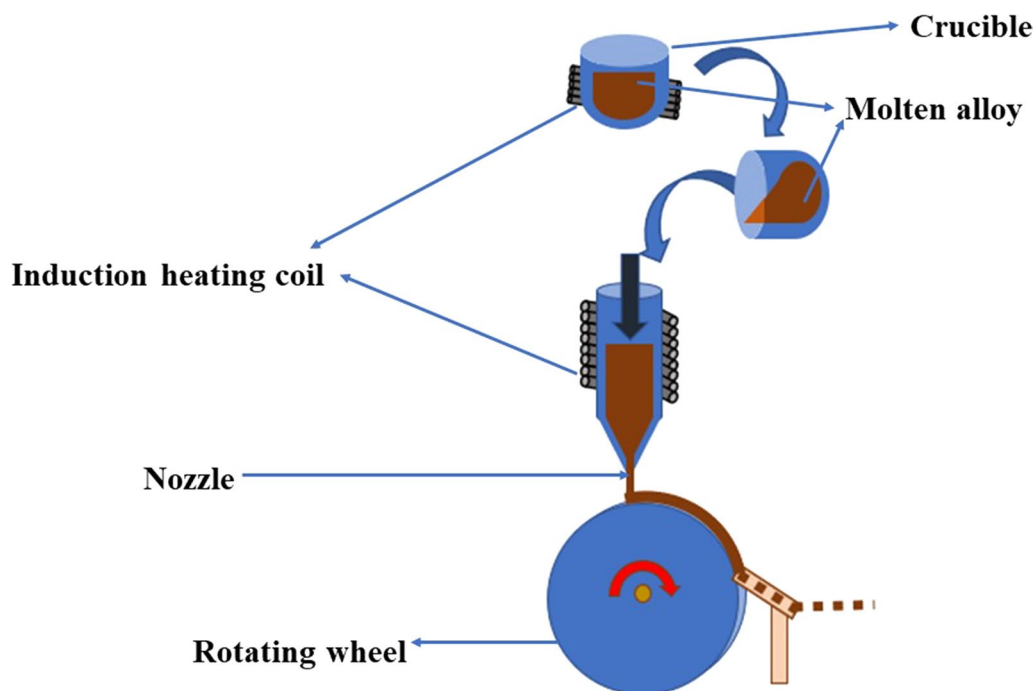

Fig. 6 Schematic representation of melt spinning technique.

the compound is liquefied in the crystal puller furnace. The cooling is done very slowly at a specific rate (2°/3° per min), and the pulling is also done simultaneously. The ampoule holding a grown ingot of a single crystal (25 mm) is taken out of the furnace, separated from the ampoule, and cut into anticipated dimensions for measurements and characterization. In some specific systems, post-treatment, the cooling rate is optimized for growing a single crystal ingot to regulate the size and morphology of single crystals.

The melt growth technique can be classified based on heating source, including arc, eddy current, and electrical resistance such as arc melting, induction melting, levitation melting, and Bridgeman technique. Figure 7 shows the schematic diagram of the melt growth technique. Some of the reported compounds prepared from the melt growth technique are given in Table I.
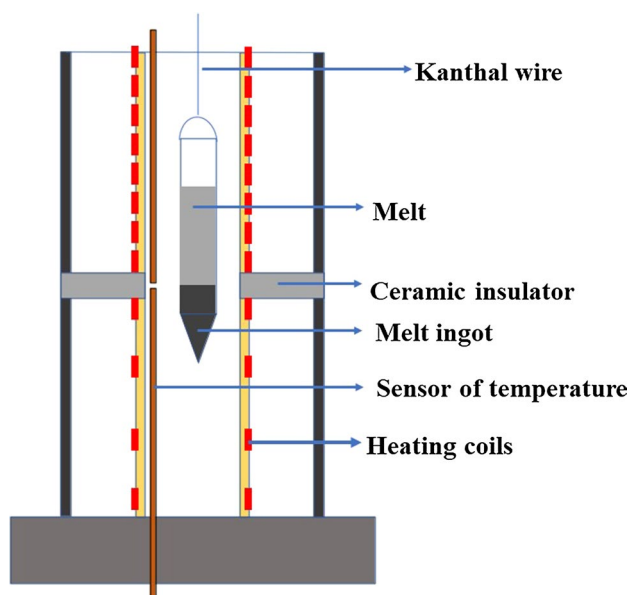
Fig. 7 Schematic representation of melt growth technique.

Sintering and Consolidated Synthesis

A proper sintering process can attain a compaction of crystallite size and stabilization of the primary phase under appropriate conditions. The compressed samples have better crystallinity and specific shape and are used for characterization and measurements. Sintering is the process that precedes the fabrication of bulk compounds. Various special positive effects on the thermoelectric properties of the materials can be gained through hot pressing (HP) and spark plasma sintering (SPS).[105]

Over the past decade, SPS has brought a nanostructure dimension to the polycrystalline bulk materials. In SPS, a die with loaded powder is sandwiched between two punches and positioned in displaced graphite plates. To achieve an excellent electrical connection, the punch and the powder are inserted by graphite papers.[104–106] By applying direct current at low voltage and high current (1–10 kA), at the rate of 1000°C min^{-1}, Joule heat is generated with uniaxial pressure loaded to enable compression. Hence, the inherited nanostructures are manufactured using a reduced ingot and refined grains of powder to obtain better performance of thermoelectric materials with less thermal conductivity.[95,107] Some of the reported thermoelectric materials are given in Table I. The steps involved in the sintering technique are shown in Fig. 8.

Hot Extrusion Method

High-purity precursors like Bi, Te, and Se are weighed stoichiometrically. The powder is manufactured by high-frequency introduction under an argon atmosphere in a graphite crucible at a temperature of 200°C. N$_2$ gas is introduced into the chamber operating at a pressure of 1.2 MPa. A conventional mechanical sieving technique measures the size distribution of the powder. To remove the oxygen from the powder surface, atomized gas powder is reduced at 360°C for 4 h. The consolidated alloy powder is compacted using Al alloy for 1 h at 450°C. None of the extruded bars showed
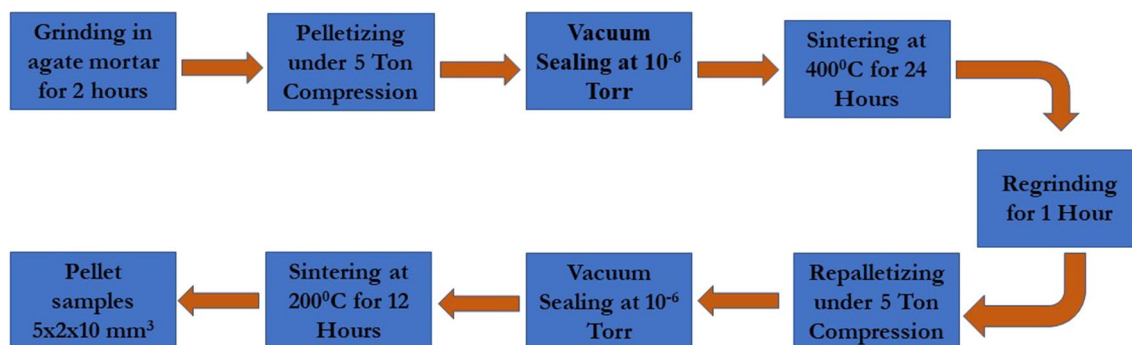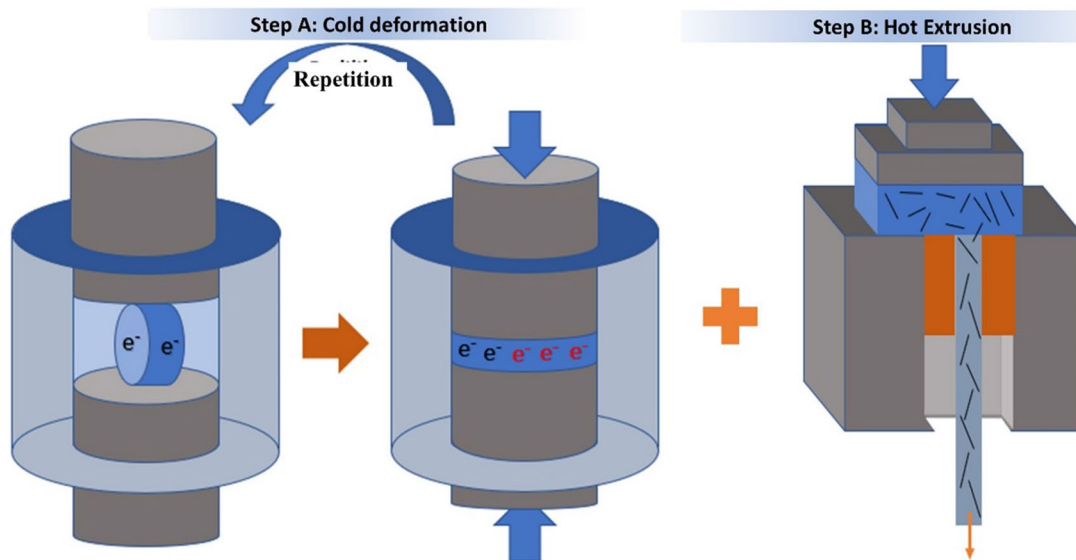

Fig. 8 Steps involved in sintering and consolidation technique.

Fig. 9 Schematic diagram of the hot extrusion process.

blistering or cracking on the surface. The density of the hot-extruded compounds was measured using the Archimedes principle. A schematic diagram of the hot extrusion process is shown in Fig. 9.

Crystal Structure

The crystal structure of prepared chalcogenides of bismuth telluride and bismuth selenides are found to crystallize in the tetradymite crystal structure.[133] A rock salt structure is observed between Bi, Te, and Se. The associated valences of Bi^+ (s^2p°) and Te^{-2} are indicated by the differences in the electronegativity among Bi, Te, and Se. Removing the metal layer of every adjacent packed plane forms a rhombohedral structure of tetradymite IV and V semiconductor.[119,134] Quintuple stalk sequences of Te–Bi–Te and Se–Bi–Se are formed in Bi_2Te_3 and Bi_2Se_3, respectively. The numbers in parentheses differentiate equivalent Te and Se sites. Bonds between the Te, Se, and Bi are polar covalent bonds, where weak van der Waals bonding exists between $Te^{(1)}$–$Te^{(1)}$ and $Se^{(1)}$–$Se^{(1)}$ atoms.[38,135,136] As a result, there is an easy cleavage for the basal planes of a and c directions.

The doping of Se in the site of tellurium does not result in any substantial structural change in the material, but there is a shift to the higher angle 2θ side with increasing content of Se atoms. This indicates the suitable incorporation of Se into the matrix of Bi_2Te_3. As a result, there is a variation in lattice constant, which was reported by Pan et al..[137] The crystal structure of Sb-doped Bi_2Te_3 attained a small particle size with better crystallinity.[138] A significant alteration of the intensity of X-ray diffraction (XRD) patterns

and peak shifting was observed in the hybridized method of BM+SPS.[55] There was no significant deviation in the XRD patterns observed in the SHS method, as the relative density of the sample was greater than 98%, but the crystallinity was poorer than the MG technique.[139] The surface morphology of the compound was found to exhibit a parallel set of cleavage planes consistent with the orientation factor. A change in the lattice parameters of indium- and selenium-doped bismuth telluride was found with an increase in lattice compressive strain.[50,51] No impurity was observed in as-synthesized samples of Bi_2Te_3 prepared by rational nanostructure design, as reported by Min et al.[140] Specific reports are available on the thermoelectric properties of ball-milled powder of bismuth antimony telluride, where the single-phase XRD patterns were obtained with a rotation speed of 150 rpm with no impurity peaks.[141]

Thermoelectric Properties

High semiconducting behavior is required to develop a perfect, optimized thermoelectric material of both p and n type with comparable performance. Yan et al.[142] found that excess electrons introduced into the lattice by deformation led to a donor-like effect. Bi atoms occupying Te sites were diffused back towards the original sublattice, and excess Te vacancies were produced.

The deformation effect was also examined for the compound Bi_2Se_3–Bi_2Te_3. It was observed that there is an unusual reduction in the electrical resistivity of cold-pressed samples. But the Seebeck coefficient was found to be within the intrinsic range due to low carrier concentration.

Preparation of the Bi_2Te_3-rich side of Bi_2Te_3–Bi_2Se_3 via zone melting and the hot-pressing method was investigated by Heon et al. to determine the thermoelectric properties.[143] The zone-melted ingot was found to be affected by the dopant, as the ingot composition is constant, whereas thermoelectric properties of hot-pressed material are related to variation of the carrier concentration caused by the generation of electronically active defects from many sources. When the content of Se was less than 4 wt.%, the highest thermoelectric figure of merit was found to be 0.3.

Bi_2Te_3–Bi_2Se_3–Sb_2Te_3 of a quasi-quaternary solid solution form showed a ZT of 1.1 at 300 K. The composite system has low carrier concentration due to non-ignorable intrinsic excitation. The electrical conductivity and Seebeck coefficients increase with the content of Sb_2Te_3. Because of the suppressed bipolar conduction, there is a decrease in the lattice thermal conductivity in an $x = 0.1$ zone-melted (ZM) ingot compared to an $x = 0$ ZM ingot.[144] An intrinsic point defect-based bismuth telluride compound showed a decrease in electrical conductivity in a low-temperature regime, whereas severe intrinsic excitation in the high-temperature region beyond 350 K caused a turnover of electrical conductivity. It was found that mechanical sintering has a significant impact on the donor-like effect.[40] The p-type chemical composition of $x = 0$, 0.05, 0.16, 0.20, 0.25 $(Bi_2Te_3)_x(Sb_2Te_3)_{1-x}$ is fabricated by zone melting. The increase in the composition of Bi_2Te_3 in Bi–Sb–Te lowers the concentration of holes systematically with the highest ZT, which was found to be 1.14 at 350 K.[145] High-energy ball milling was carried out for n-type Bi_2Te_3 bulk compound followed by spark plasma sintering, which contributed to the uniformity of the grains and grain boundaries in the materials, thus resulting in increased thermoelectric properties with the highest ZT value of 1.2 at 480 K.[146] The parallel and perpendicular directions of electrical resistivity of the reduced of pretreated powder were found to decrease by 25% and 15%, respectively, as compared to dry powder samples. There was also an enhancement of Seebeck coefficient by 115% at room temperature for reduced pretreated powder in the perpendicular direction compared to dry powder sample, with a ZT of 0.1 at 500 K.[147]

In order to investigate the effect of graphene nanoparticle structural integrity on the thermoelectric properties, $Bi_2Te_{2.7}Se_{0.3}$/graphene composites were prepared by Faraha et al.[148] through ball milling and spark plasma sintering techniques. The electrical conductivity of samples with higher graphene concentration was found to be low due to the agglomeration and increased scattering of charge carriers. As the milling time of graphene was increased, the appearance of large defects and low structural integrity was noted, with an improved Seebeck coefficient. The electronic part controlled the thermal conductivity of the samples because of the high electrical conductivity of the optimized samples.

However, a noticeable reduction in the lattice thermal conductivity was observed due to the enhanced scattering at the interfaces. As a result of graphene addition, ZT was found to increase in the composite samples compared to pristine $Bi_2Te_{2.7}Se_{0.3}$. $Bi_{0.3}Sb_{1.7}Te_{3.0}$, thermoelectric compound was fabricated using an yttrium vessel and stainless steel vessel by Mongkol et al.[149] The mixture milled at 150 rpm with an yttrium vessel was found to have a higher ZT value than the compound milled in a stainless steel vessel by a factor of 1.7 at 500 K. The electrical conductivity, Seebeck coefficient, and thermal conductivity of the bismuth antimony telluride were 4.6×10^4 S/m, 295 µV/k, and 0.94 W/mK, respectively, at 500 K (Fig. 10a, b, c, and d).

The mechanochemical method of producing nanostructured bismuth antimony telluride with added silicon carbide and alumina nanoparticles was reported by Shyam et al.,[150] which showed a gradual decrease in the Seebeck coefficient from 0.05 mW/K to 0.04 mW/K at around 310° C. In this investigation, (p-type) $Bi_{0.3}Sb_{1.7}Te_{0.3}$ thermoelectric compounds were synthesized at various ball-milling speeds using yttrium balls. The powder milled at 150 rpm exhibited a single-phase XRD pattern with a sintered temperature of 350°C. The grain size was found to be approximately 1 µm at the fractural surface, and the ZT of the compound was about 1.0 at 350°C. Another study investigated the preparation and thermoelectric performance of BiSbTe thermoelectric materials fabricated at different ball-milling speeds with yttria-stabilized zirconia ceramic balls and vessels.[151] The study of ruthenium composite revealed a certain mass fraction range and an increase in the content of Ru nanoparticles with local grain refinement. The thermoelectric properties were enhanced by low energy carrier filtering and a wide range of phonon scattering. The investigation also explored optimization of second-phase thermoelectric properties of nanoparticles with ZT of 0.86 at 420 K.[152] Recently, boron- and indium-doped $Bi_{0.48}Sb_{1.52}Te_3$ thermoelectric compounds were synthesized through the zone-melting method by Wang et al.[153] The synergistic effects yielded a maximum ZT of 1.45 at 350 K and a power factor of 41 µW/Cm K^2 in $Bi_{0.48}Sb_{1.51}5In_{0.005}Te_3 + 0.6$ wt.% boron-doped samples (Fig. 11a, b, c, and d). In our recent research work,[126] a considerable reduction in electrical resistivity was found in $(Bi_{0.96}In_{0.04})_2Se_{2.7}Te_{0.3}$, leading to an increase in the power factor (1900 µW/mK^2) and ZT (0.28) by a factor of about 8.0 and 4.1, respectively, compared to Bi_2Se_3 (Fig. 12a, b, c, and d).

Along with the melt growth and ball milling technique, the melt spinning technique has witnessed an influence on the properties of chalcogenide thermoelectric materials.[154] The influence of the density of states and microstructure decomposition of spinodal microscale on water-quenched 0.1 wt.% PbTe was investigated by Jaquat et al.[155] The cooling rate modified fundamental properties like electrical
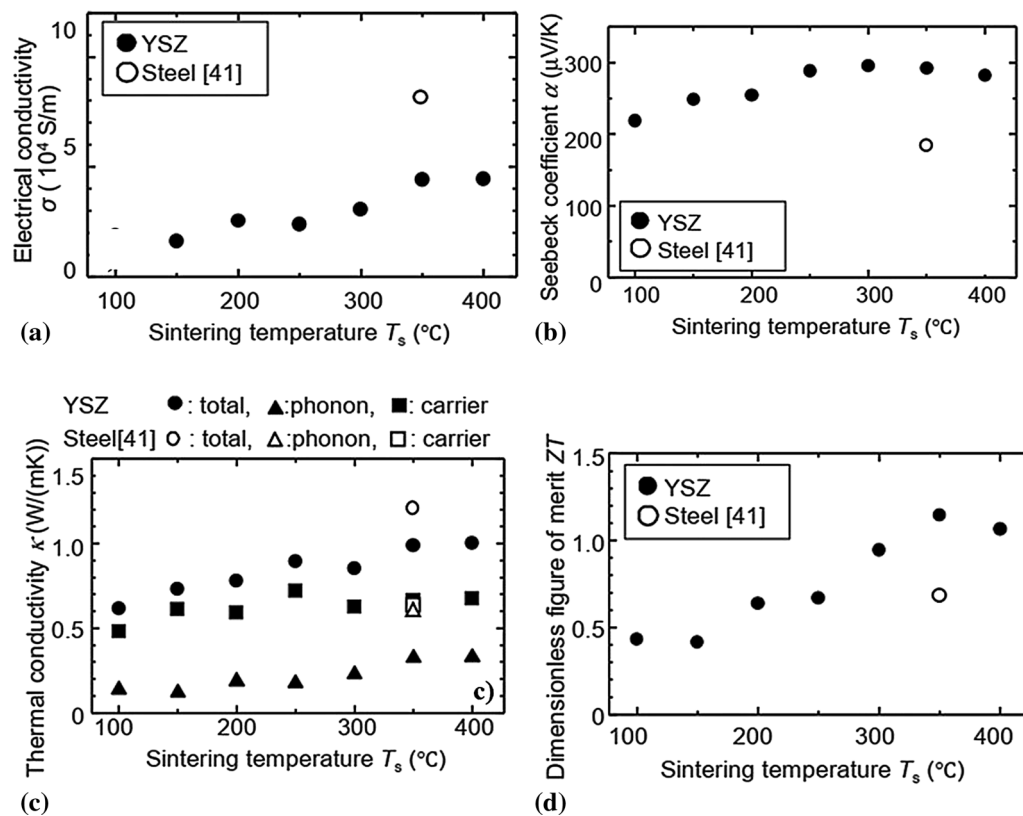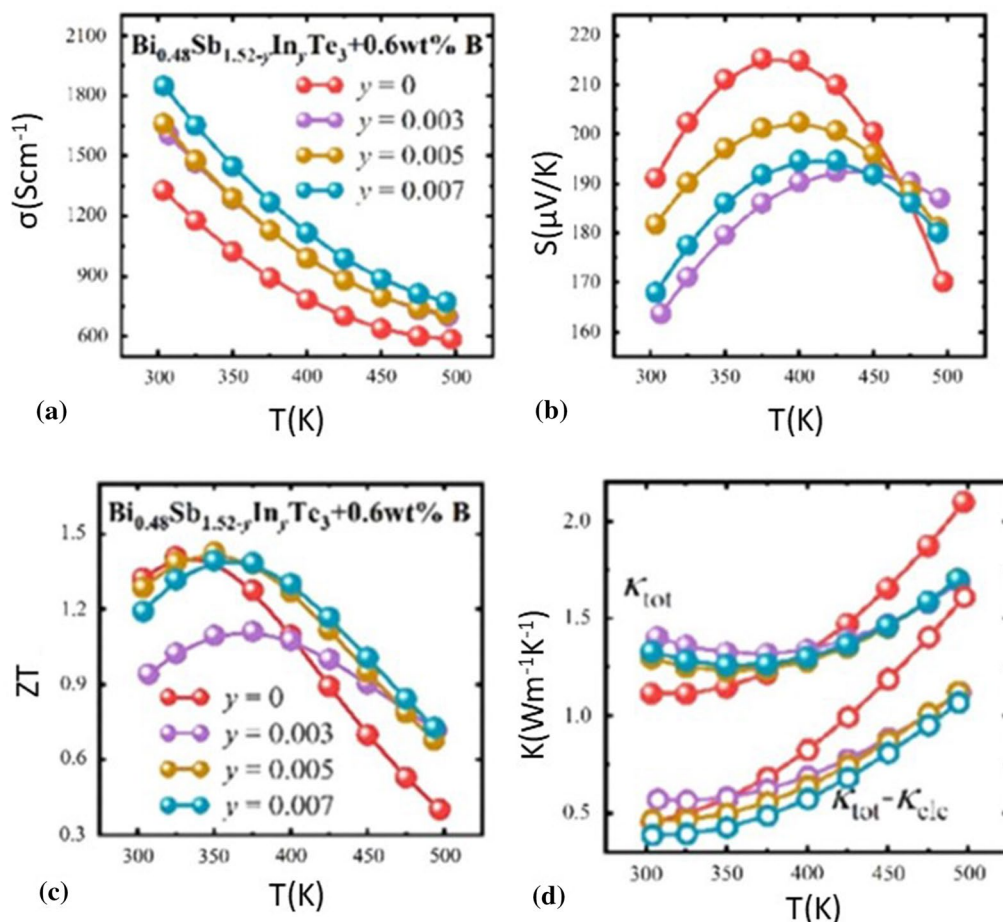
Fig. 10 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of bismuth antimony telluride. Reprinted from *Ceramics international*, 46, M. Bumrungpon, K. Hirota, K. Takagi, K. Hanasaku, T. Hirai, I. Morioka, R. Yasufuku, M. Kitamura, and K. Hasezaki, Synthesis and thermoelectric properties of bismuth antimony telluride thermoelectric materials fabricated at various ball-milling speeds with yttria-stabilized zirconia ceramic vessel and balls, 13869. Copyright (2020), with permission from Elsevier.[149]

resistivity and thermal conductivity. As a result, the obtained *ZT* of PbTe was found to be 0.8 at 300 K. The thermoelectric properties of Cu-doped p-type $Bi_{0.5}Sb_{1.5}Te_3$ were investigated to determine the intrinsic excitation effect in BST material, resulting in the highest *ZT* of 1.0 at 450 K.[156] The layered compound $BiMnTe_4$ was found to be a p-type semiconductor with a high Seebeck coefficient at 300 K (168 µV/K). Also, in nanostructured $Bi_2Te_3/MnTe_2$, the *ZT* was found to be 0.26 at 480 K.[157] The sintered bulk materials of p-type $Bi_{0.52}Sb_{1.48}Te_3$ prepared using melt spinning and rapid sintering were found to depend on thermal conductivity of ambient gases with enhancement in *ZT* value of about 1.09 at 340 K.[158] To control the crystallographic preferred orientation, melt spinning method has been applied for CHI_3-doped $Bi_2Te_{2.4}Se_{0.6}$ alloys with an optimized frequency of 300 rpm with *ZT* of 1.02 at 400 K.[119] The outstanding homogeneity and reproducibility by varying the stoichiometry have played a crucial role in the transport properties of p-type $Bi_xSb_{2-x}Te_3$ prepared by melt spinning.[159] The bulk materials of p-type $Bi_{0.52}Sb_{1.48}Te_3$ were synthesized by Yun et al.,[160] and it was observed that an argon atmosphere could effectively inhibit heat loss

and suppress the sublimation of tellurium. Therefore, the $Bi_{0.52}Sb_{1.48}Te_3$ sample showed the highest *ZT* of 1.09 at 340 K (Fig. 13a, b, c, and d). The secondary phase of $NiTe_2$ and $NbTe_2$ in a p-type $Bi_{0.5}Sb_{1.5}Te_3$ thermoelectric was investigated by Kim et al.[161] $Bi_{0.5}Sb_{1.5}Te_3(NiTe_2)_{0.01}$ and $Bi_{0.5}Sb_{1.5}Te_2(NbTe_2)_{0.01}$ exhibited a *ZT* of 0.98 and 0.94 at 300 K, respectively (Fig. 14a, b, c, and d).

The SHS technique is a combustion method for synthesizing thermoelectric materials. It was systematically evaluated by varying the thermodynamic and kinetic parameters for n-type $Bi_2Se_{2.4}Te_{0.6}$ with reduced cost. A *ZT* of 0.95 was observed at 424 K and was 25% greater than melt-grown samples.[125] Bulk samples of n-type Bi_2Te_3 fabricated by stacking 75 layers on top of each other has shown an electrical conductivity of 122 S cm^{-1}, Seebeck coefficient of -105.7 µV/K, and a *ZT* of 0.3 at 450 K.[113] An investigation of the thermoelectric performance of $Bi_2Se_{3-x}Te_x$ ($x =$ 0, 0.3, 0.6, 0.9 and 1.5) prepared by SHS reported a power factor of 11 µW/mK. The thermoelectric figure of merit was found to be enhanced by the low lattice thermal conductivity and calculated to be 0.67 at 483 K for $Bi_2Se_{1.5}Te_{1.5}$.[162] Further, a self-propagating high-temperature technique was
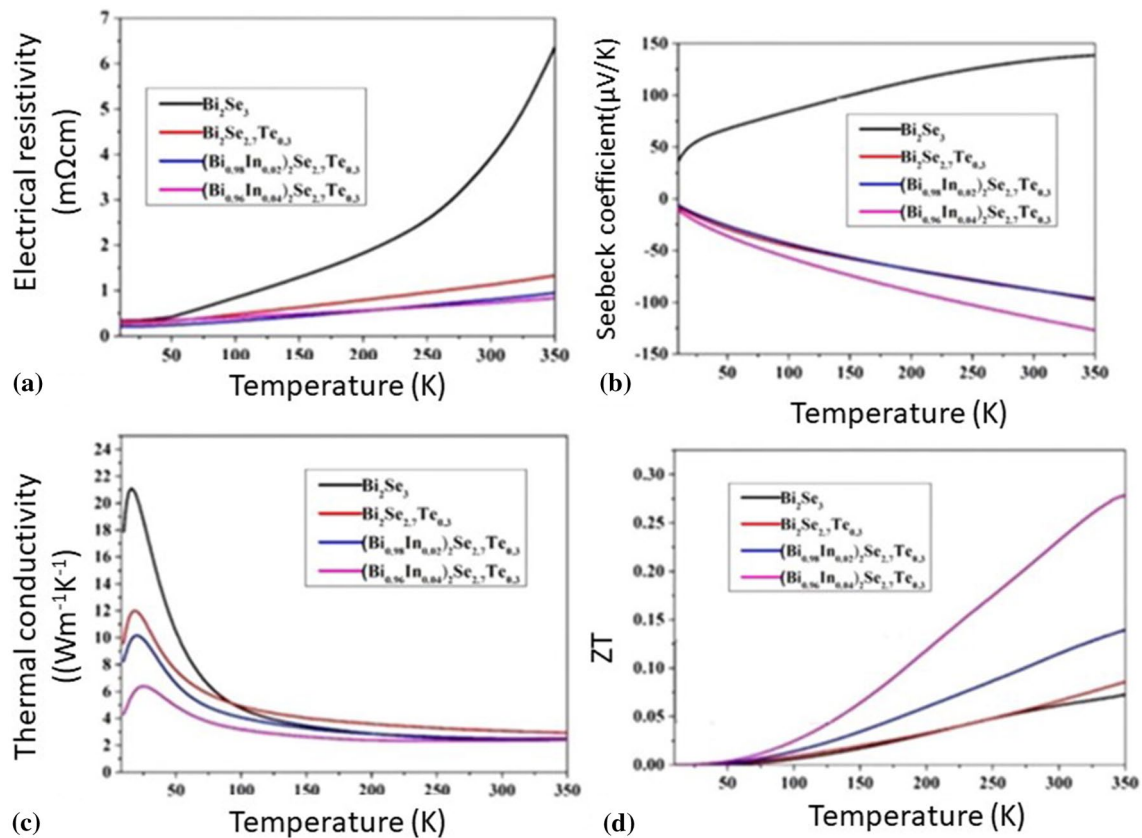
Fig. 11 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) *ZT* value, and (d) total thermal conductivity of $Bi_{0.48}Sb_{1.51}5In_{0.005}Te_3 + 0.6$ wt.% boron-doped samples. Reprinted from *Chemical Engineering Journal*, 429, H. Wang, G. Wu, Z. Yan,

X. Tan, J. Cai, H., Peng, S., Liu, G Jiang, Synergistic Effects of B-In Codoping in Zone-Melted $Bi_{0.48}Sb_{1.52}Te_3$-Based Thermoelectric, 130381, Copyright (2021) with permission from Elsevier.[153]

used to prepare $Bi_2Se_{3-x}Te_x$, where Se vacancies and antisite defects resulted in a carrier concentration of 2×10^{19} cm^{-3}. Hence, there is a suppression in lattice thermal conductivity from 1.07 W/mK to 0.61 W/mK at 300 K, and a *ZT* of 0.67 at 473 K has been achieved for $Bi_{0.5}Sb_{1.5}Te_3$.[163] Textured $BiSbTe_{1.5}Se_{1.5}$ was prepared by Oleg et al.[164] They achieved a maximum *ZT* of 0.43 at 500 K using self-propagation high-temperature technique. The texturing resulted in anisotropy in the specific electrical conductivity and thermal conductivity, as represented in Fig. 15a, b, c, and d.

Single-phase nanopowders were synthesized using the hydrothermal method where $BiCl_3$ and $SbCl_3$, and Te powders were used as precursors. The presence of a thermal difference probably enhanced the directional arrangement of nanosheets of $Bi_{0.5}Sb_{1.5}Te_3$, which is advantageous for improving the thermoelectric properties. The highest figure of merit was found to be 0.86 at 373 K.[165] The Seebeck coefficient of prepared polythiophene (P_{Th})/Bi_2Te_3 was determined to be negative over the whole temperature range, and

the highest value was found to be 130 µV/K. The decrease in carrier concentration and electrical resistivity was due to the poor conductivity of the polymer, which resulted in a *ZT* of 0.17 at 473 K.[166] A widely used and facile hydrothermal approach was carried out for bismuth telluride nanorods with nanoplates stacks. Based on the titration, composition of the alloys was determined to be $Bi_2Te_{2.4}$. The two types of sintering technologies of high pressure/high-temperature (HPHT) and SPS were organized to prepare a Bi_2Te_3 alloy, which shows ZT values of 0.47 and 0.42 for HPHT and SPS, respectively, at 430 K.[167] Besides, the thermoelectric properties of nanostructured La-doped Bi_2Te_3 compound prepared by hydrothermal technique were investigated. The compound exhibited a flower-like structure due to the assembly of nanosheet crystals. The defects strongly affected the compound, and the highest *ZT* value of 0.4 at 550 K was shown by the pristine sample.[168] Bismuth telluride is assembled by nanosheets and synthesized by solvothermal route. The large compatible plane structure, reduction of nucleation, and
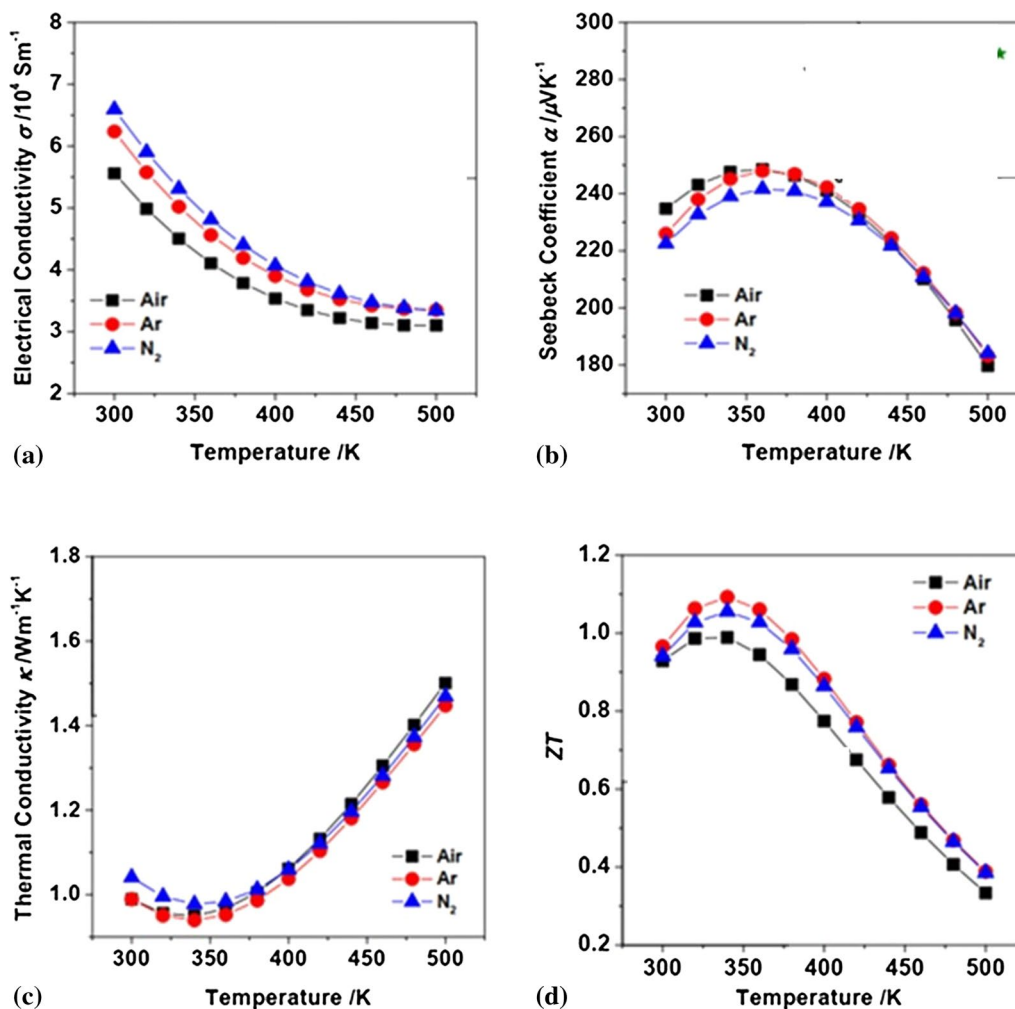
Fig. 12 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of single-crystal $(Bi_{0.96}In_{0.04})_2Se_{2.7}Te_{0.3}$ samples. Reprinted from *Journal of Alloys and Compounds*, 866, G. S. Hegde, A. N. Prabhu, Y. H. Gao, Y. K. Kuo, and V. R. Reddy, Potential thermoelectric materials of indium and tellurium co-doped bismuth selenide single crystals grown by melt growth technique, 158814, Copyright (2020) with permission from Elsevier. [126]

interfacial angle energies are responsible for the generation of defects. Hence, to assess the influence of the defects on their thermoelectric performance, bulk pellets were examined, and they showed a *ZT* value of 0.68.[169] Rini Singh et al. demonstrated an easy and economical wet chemical route for the preparation of bismuth telluride nanostructures. Bismuth telluride was studied with only preliminary investigations; the samples exhibited rhombohedral (R-3m) and hexagonal (P-3 m1) phases. All the XRD peaks could be indexed well with Bi_2Te_3 and BiTe phases. Some of the peaks represent the formation of oxide. The nanocrystals of Bi_2Te_3 were fabricated using a colloidal nanoplate technique. The crystals exhibited a highest power factor of 0.35 m Wm^{-1} K^{-2} at 433 K, which is among the highest reported values for flexible thermoelectric films.[170] High-purity bismuth telluride (Bi_2Te_3) nanostructures have been synthesized using coprecipitation and annealing process. The study of thermoelectric properties of Bi_2Te_3 nanostructure in synthesis (HNO_3-Bi&Te) showed a maximum value of thermoelectric voltage of 21 mV at a temperature difference of 90 K. The amount of *ZT* obtained in the co-precipitated bismuth

telluride was found to be enhanced by 6.5 times compared to the annealing method.[171]

Bi_2Te_3 nanoparticles were fabricated by a microwave-assisted chemical synthetic route with tartrate complexes Bi^{3+} and Te^{4+}. The nanoparticles exhibited a higher Seebeck coefficient (-135 μVK^{-1}), lower thermal conductivity (0.957 W/mK), and a dimensionless figure of merit of 1.0 at 300 K.[172] The effect of microwave processing was examined to determine the optimal thermoelectric performance of $(Bi_xSb_{1-x})_2Te_3$/ethylene glycol 2964 (EG) alloy at room temperature. EG insertion enhanced the Seebeck coefficient, and a *ZT* of 1.2 was obtained at 300 K.[173] This technique was utilized in a comparative study of $Bi_{2-x}Sb_xTe_3$ prepared by mechanochemical alloying and microwave (MW) synthesis routes, where a hexagonal platelet morphology was observed. Microwave-synthesized samples showed thermal conductivity less than that obtained by the alloying method, with *ZT* values of 1.0 and 0.6 obtained at 440 K for the microwave route and mechanochemical alloying, respectively.[174] The microwave technique was also adopted to synthesize thermoelectric
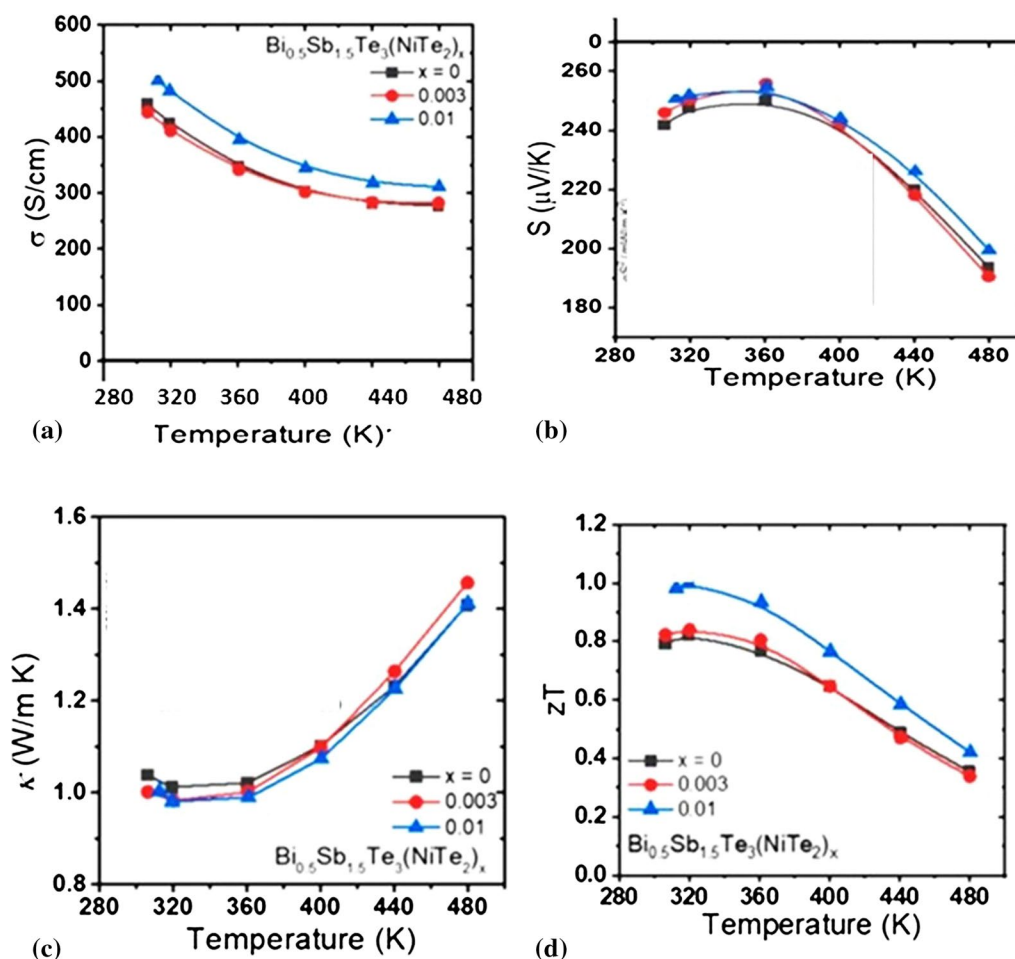
Fig. 13 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of single-crystal $Bi_{0.52}Sb_{1.48}Te_3$ samples. Adapted from *ACS Applied Materials & Interfaces*, 12, Y. Zheng, H. Xie, Q. Zhang, A. Suwardi, X. Cheng, Y. Zhang, W. Shu, X. Wan, Z. Yang, Z. Liu, and X. Tang, Unrave-ling the critical role of melt-spinning atmosphere in enhancing the thermoelectric performance of p-type $Bi_{0.52}Sb_{1.48}Te_3$ alloys, 36186. Copyright (2020) with permission from the American Chemical Society.[158]

nanopowders of a $Bi_{2-x}Sb_xTe_3$ system. A unique transition was observed from p- to n-type semiconducting with *ZT* values of 1.04 and 0.4, respectively, for the n and p types at 448 K.[175]

Ahmed et al.[176] used spark plasma sintering for the preparation of n-type $(Bi_{0.95}Sb_{0.05})_2(Se_{0.05}Te_{0.95})$. The Seebeck coefficient was found to increase by 12% relative to the sample prepared by dry conditioning. The simultaneous reduction in electrical resistivity and thermal conductivity observed in the sample prepared by SPS led to an enhanced *ZT* value (0.63 at 420 K) by 21% as compared to that of the dried mixture (Fig. 16a, b, c, and d). The spark plasma sintered thermoelectric compound $Bi_{0.5}Sb_{1.5}Te_3$ showed the lowest thermal conductivity of 0.85 W/mK, electrical conductivity of 4.48 S/cm, and the highest *ZT* of 1.03 at 300 K.[177]

Nanopowders of selenium and lutetium co-doped Bi_2Te_3 are synthesized by hydrothermal method and are sintered using spark plasma sintering technique. By doping of Se into Lu-doped Bi_2Te_3, the electrical conductivity of $Lu_{0.1}Bi_{1.9}Te_{3-x}Se_x$ material is found to decrease with the increase in Se content due to the reduced carrier concentration, while the Seebeck coefficient values are observed to be enhanced. The huge reduction in the lattice thermal conductivity of $Lu_{0.1}Bi_{1.9}Te_{3-x}Se_x$, ascribed to point defects and fluctuation of atomic mass, results in a maximum *ZT* value of 0.85 at 420 K. Powders of high entropy and single-phase nanosized $(BiSbSe_{1.5}Te_{1.5})_{1-x}Cu_x$ compound with concentration $x = 0$, 0.3, 0.6 were prepared by soft chemical reaction, due to its low thermal conductivity, and the compound was found to be favorable for thermoelectric applications.[178] Hamawandi et al.[179] reported
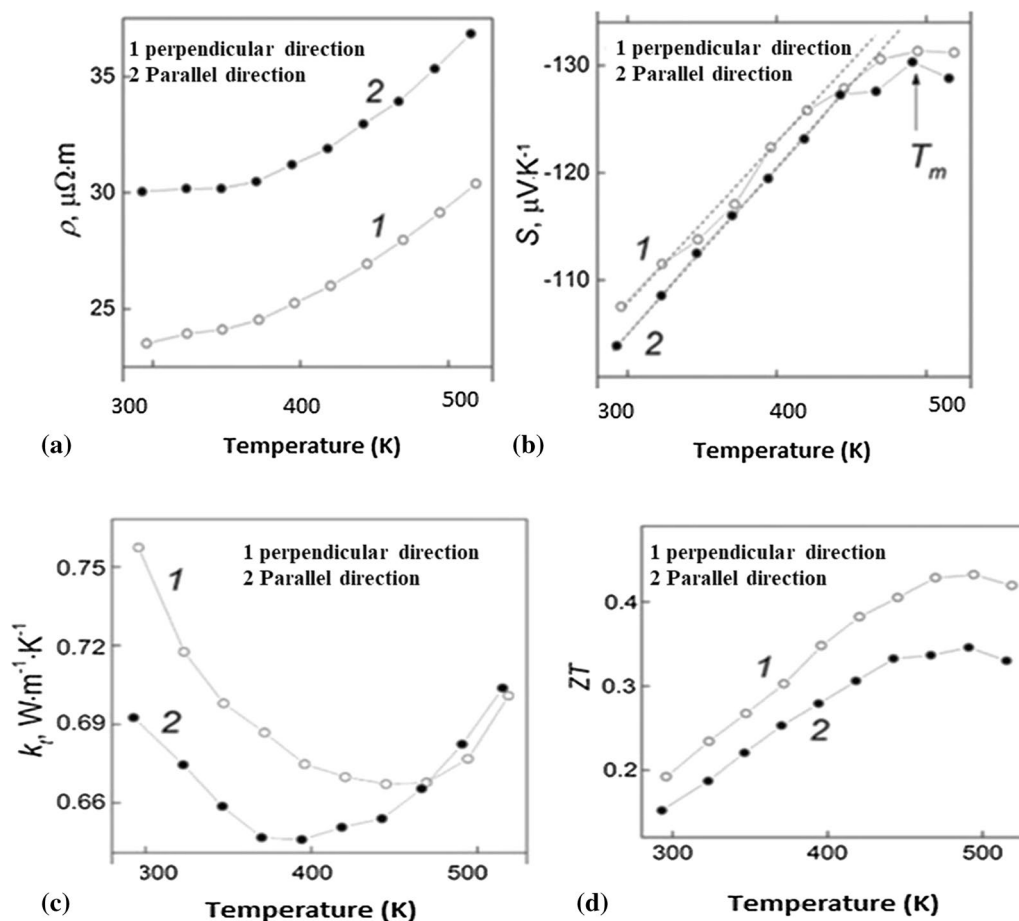
Fig. 14 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of $Bi_{0.5}Sb_{1.5}Te_3(NiTe_2)_{0.01}$. Adapted from *Applied Science*, 11, H.-S. Kim, T. Kim, J. An, D. Kim, J. H. Jeon, and S. Kim, Segregation of NiTe$_2$ and NbTe$_2$ in p-Type Thermoelectric $Bi_{0.5}Sb_{1.5}Te_3$ Alloys for Carrier, Energy Filtering Effect by Melt Spinning, 910. Copyright (2021) with permission from MDPI under CC by license.[161]

two forms of bismuth telluride synthesized by a hydro and polyol method, where the final forms of samples prepared by both methods were subjected to spark plasma sintering. Using the hydro method, the electrical conductivity values, Seebeck coefficient, thermal conductivity, and *ZT* were found to be 9.6×10^5 S/m, -149 µV/K, 0.9 W/mK, and 0.88, respectively, at 373 K, whereas they were 9.2×10^5 S/m, -148 µV/K, 0.86 W/mK, and 0.86, respectively, at 373 K using the polyol method (Fig. 17a, b, c, and d). Hong et al. synthesized the SbI$_3$-doped 95%Bi$_2$Te$_3$ and 5% Bi$_2$Se$_3$ compounds using quick solidification and extrusion between 420°C and 480°C. The hot-extruded compounds exhibited Seebeck coefficient values of 160.8, 170.2, and 165.7 mV/K at 420, 450, and 480°C respectively. The electrical resistivity for the compounds at 420, 450, and 480°C was found to be 0.49, 0.57, and 0.51 Ωm, respectively. The maximum power factor value of the compound at 480°C was 53.8×10^6 mW cm^{-2} K^{-2}.[130] Soon

lim et al. proposed the hot extrusion technique for ZnO-encapsulated Bi$_2$Te$_{2.7}$Se$_{0.3}$ alloys to determine the thermoelectric properties. The electrical resistivity, Seebeck coefficient, and *ZT* values were found to be 2×10^5 S/m, -150 µV/K, and 0.7, respectively.[131] Jung et al. introduced the hot extrusion method to fabricate high-performance n-type thermoelectric bismuth tellurium selenides. It was observed that electrical conductivity of 33,333 S/m was obtained for a sample prepared at 2.40 Mpa and 480 K, whereas the highest *ZT* value and Seebeck coefficient of 0.8 and 200 µV/K, respectively, were found at 480 K.[132] N-type $(1-x)Bi_2Te_{3-x}Bi_2Se_3$ alloys with various composition and electron density were investigated by Jung et al. using the hot extrusion method. The donor dopant used was SbI$_3$ to control the electron density of the samples in 10^{19} cm^{-3} range. 0.85Bi$_2$Te$_3$–0.15Bi$_2$Se$_3$ shows electrical resistivity, Seebeck coefficient, and power factor values

Fig. 15 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of BiSbTe$_{1.5}$Se$_{1.5}$. Reprinted from *Journal of Alloys and Compounds*, 872, O. Ivanov, M. Yaprintsev, A. Vasilev, E. Yaprintseva, Micro-structure and thermoelectric properties of the medium-entropy block-textured BiSbTe$_{1.5}$Se$_{1.5}$ alloy, 159743. Copyright (2021) with permission from Elsevier.[164]

of 300,000 S/m, -300 μV/K, and 3.5×10^{-3} W/mK^2, respectively.[180]

Effect of Point Defect and Effective Mass (*m**) on Carrier Transport Phenomenon and Density of States (DOS)

Bismuth chalcogenide compounds have two primary defects, lines and points in the lattice, as an effect of quenching. The line defect is considered to be dislocation, which decreases the mobility of the charge carriers. Further, single crystals are tilted strongly through the parallel axis to the basal plane. The point defect generated at high temperature during sintering or growth can be quenched in the sample at a lower temperature. The point defects in chalcogenide compounds are mainly of three types: (a) Frankel defect (b) Schottky–Wagner defect, and (c) antistructure defect. These defects can act as an acceptor/donor with regard to the levels of energy associated with the Fermi level. In bismuth chalcogenides, the acceptor levels lie in the valence band, and donor levels lie in the conduction band. As a result, the defects are subjected to ionization throughout the temperature range. The impact of vacancies formed through plastic deformation in n-type Bi$_2$Te$_3$ and Bi$_2$Se$_3$ decreases the mobility of carriers while leaving the charge carriers unaffected due to ionized vacancy scattering. Ionization is established by the bond rearrangement of electrons rather than the trapping of conduction holes and electrons.[181] Point defect engineering is an effective tool for enhancing thermoelectric bismuth chalcogenide-based alloys by regulating the content of dopants like Sb, In, and Sn in Bi$_2$Te$_3$ and Bi$_2$Se$_3$ based on minor differences in electronegativity.[70]

In some cases, the effective mass of a material results in higher valley degeneracy at a low- to near-room-temperature range. The significant contribution to carrier transport comes from the position of the Fermi level (E_F) from the conduction energy band (E_C) in an n-type semiconductor and the
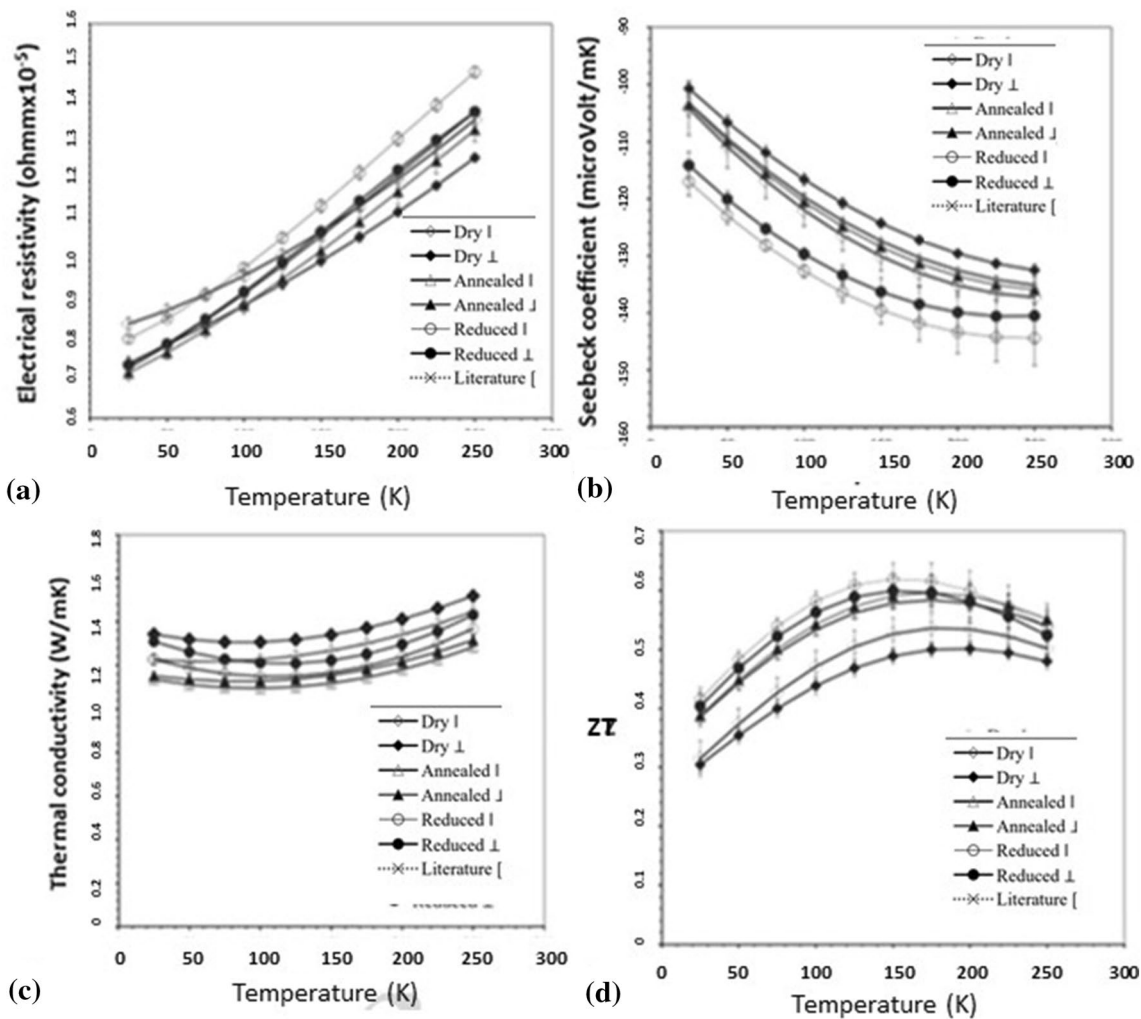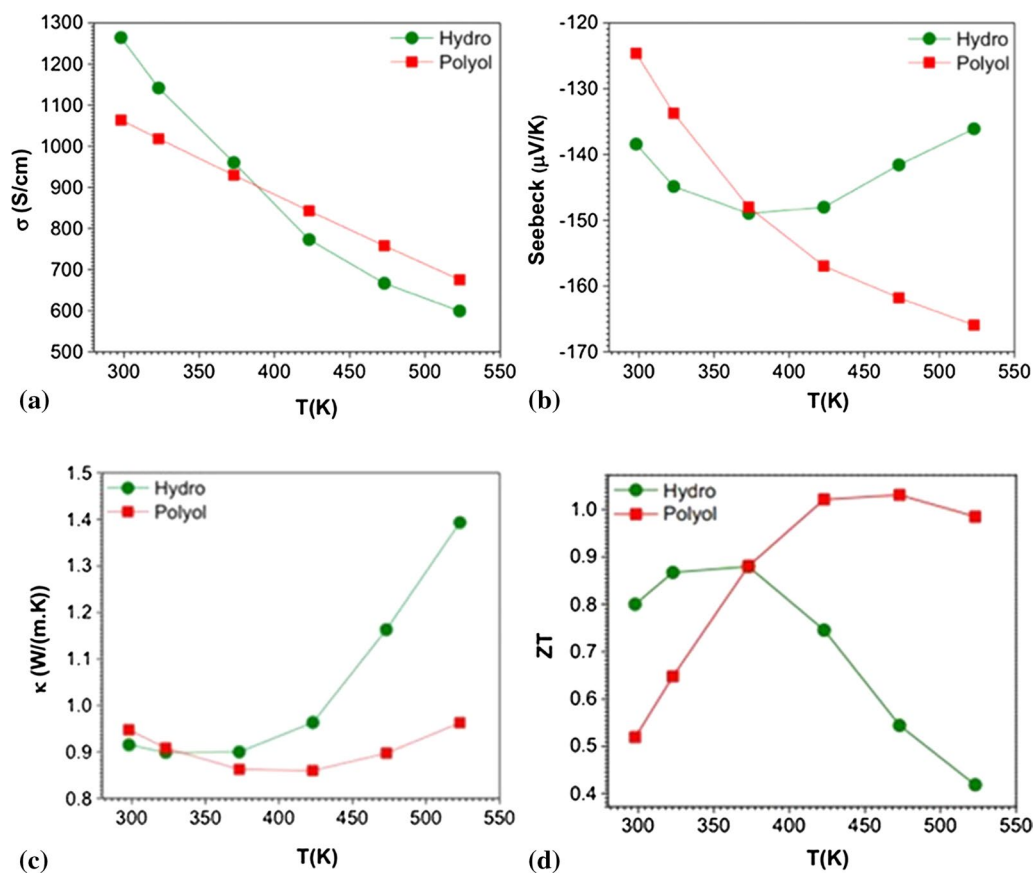
Fig. 16 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of $(Bi_{0.95}Sb_{0.05})_2$ $(Se_{0.05}Te_{0.95})$. Reprinted from *Journal of Alloys and Compounds* 874, A. A. Abdelnabi, V. Lakhian, J. R. McDermid, The effect of powder pre-treatment on the mechanical and thermoelectric properties of spark plasma sintered N-type bismuth telluride, 159782. Copyright (2021) with permission from Elsevier.[176]

valence energy band (E_v) in the case of a p-type semiconductor. Thermoelectric power increases with an increase in $E_C–E_F$, which helps increase weighted mobility and thermopower. The substitutional alloys display a larger energy gap than binary compounds by suppressing minority charge conduction at high temperatures. The high weighted mobility in bismuth chalcogenides is mainly due to its complex Fermi surface, which generates six valley conducting bands.[182]

Burai Quantum ESPRESSO software is used to determine the density of states (DOS) and Fermi energy of Bi_2Te_3, Bi_2Se_3, and In/Sb/Sn-doped $Bi_2Te_{2.7}Se_{0.3}/Bi_2Se_{2.7}Se_{0.3}$. The simulated DOS of Bi_2Te_3 and Bi_2Se_3 are shown in Fig. 18a and b, which shows the electronic contribution from several atoms. The valence band is basically controlled by the 5p state of the tellurium atom. The conduction band comprises both 6p Bi and 5p Te states with short tight bonds. First,

the second and fourth atomic layers have zero density of state and have a gap in the Fermi level.[183] Each atom of Bi_2Te_3 and Bi_2Se_3 participates in the formation of a Dirac cone. P_z states of bismuth atoms have the greatest influence on the formation of the surface state with linear dispersion, whereas a minor contribution is observed from selenium and tellurium atoms in p_x and p_y orbitals. The density of states provides evidence regarding the derivation of bands in the instance of Bi_2Te_3. The s orbital of Bi, and Te-1 and Te-2 atoms contribute the most states to core bands, while p orbitals of Te/Se-1 and Te/Se-2 contribute the most states to the valence bands. From p orbitals, the calculations of band structures and the total density of states, we obtain an energy gap value of around 6.79 eV for Bi_2Se_3; conversely, for Bi_2Te_3, the band gap is calculated as 7.0 eV (Table II). The dopant elements indium, tin, antimony (cations), and

Fig. 17 Temperature-dependent (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *ZT* value of polyol and hydro bismuth telluride. Reprinted from *Nanomaterials*, 4, Hamawandi B, Batili H, Paul M, Ballikaya S, Kilic NI, Szukiewicz R, Kuchowicz M, Johnsson M, Toprak MS, Minute-Made, High-Efficiency Nanostructured Bi_2Te_3 via High-Throughput Green Solution Chemical Synthesis, 2053. Copyright (2021), with permission from MDPI under CC by license.[179]

selenium and tellurium (anions) were selected based on their ionic radius and the similar properties of their outer shells. Sn, In, and Sb are known to be unique cases of resonant impurities in Bi_2Te_3 and Bi_2Se_3 semiconductors.[184] The doping of different elements causes a rigid shift of the Fermi level. The resonance level (RL) has different effects on the electronic and transport performance of a base compound, depending on its position and band edges, and it acts as a charge trap when it is in the strong resonant scattering center. These alloys form defect states pin the Fermi level and promote the partial charge localization. By considering the perspective of semiconductors based on thermoelectric materials, the RL is close to the band edge and hybridizes with the host electronic states around a valence band. Therefore, this condition could increase the Seebeck coefficient and *ZT* value of the materials. It is noted that high defect states are the cause for the acceptor-like behavior of dopants In, Sn, and Sb in bismuth.[185]

From Fig. 18c and d, it is realized that the energy peak at −0.96 is primarily created by indium 5*s* and 6*p* states of bismuth. The s-state of Bi receives few electrons from indium in the DOS region of 1.5 eV. At the resonance level, the impurity state coincides with the band energy of the host atoms, unlike the normal dopant state, where the impurity energy falls within that resonant peak in the valence band. This can be attributed to the s orbital of the dopant. The density of states of Sb-doped $Bi_2Te_{2.7}Se_{0.3}$ and $Bi_2Se_{2.7}Te_{0.3}$ has been shown in Fig. 18e and f. In order to fill sp^3d^2 hybrid, an electron from the p orbital of Te [(1)] and Se [(1)] shifts to the Bi metal atom. The sharp resonant peak is observed at 0.95 eV of the DOS near the edge of the valence band in Sn-doped $Bi_2Te_{2.7}Se_{0.3}$, whereas, *s*-like behavior is observed in the orbital moment of the DOS peak. The resonant level is formed in the 5s orbital of Sn, as shown in Fig. 18g and h.[186] With progression of the DOS and Fermi level with insertion of Sn concentration and Se/Te, n–p crossover takes place. Therefore, Sn compensates the donor vacancy effect. Hence, by observing these phenomena, it seems that the effective way of controlling the Fermi level is co-doping. The theoretically simulated Fermi energy has been calculated and given in Table II.
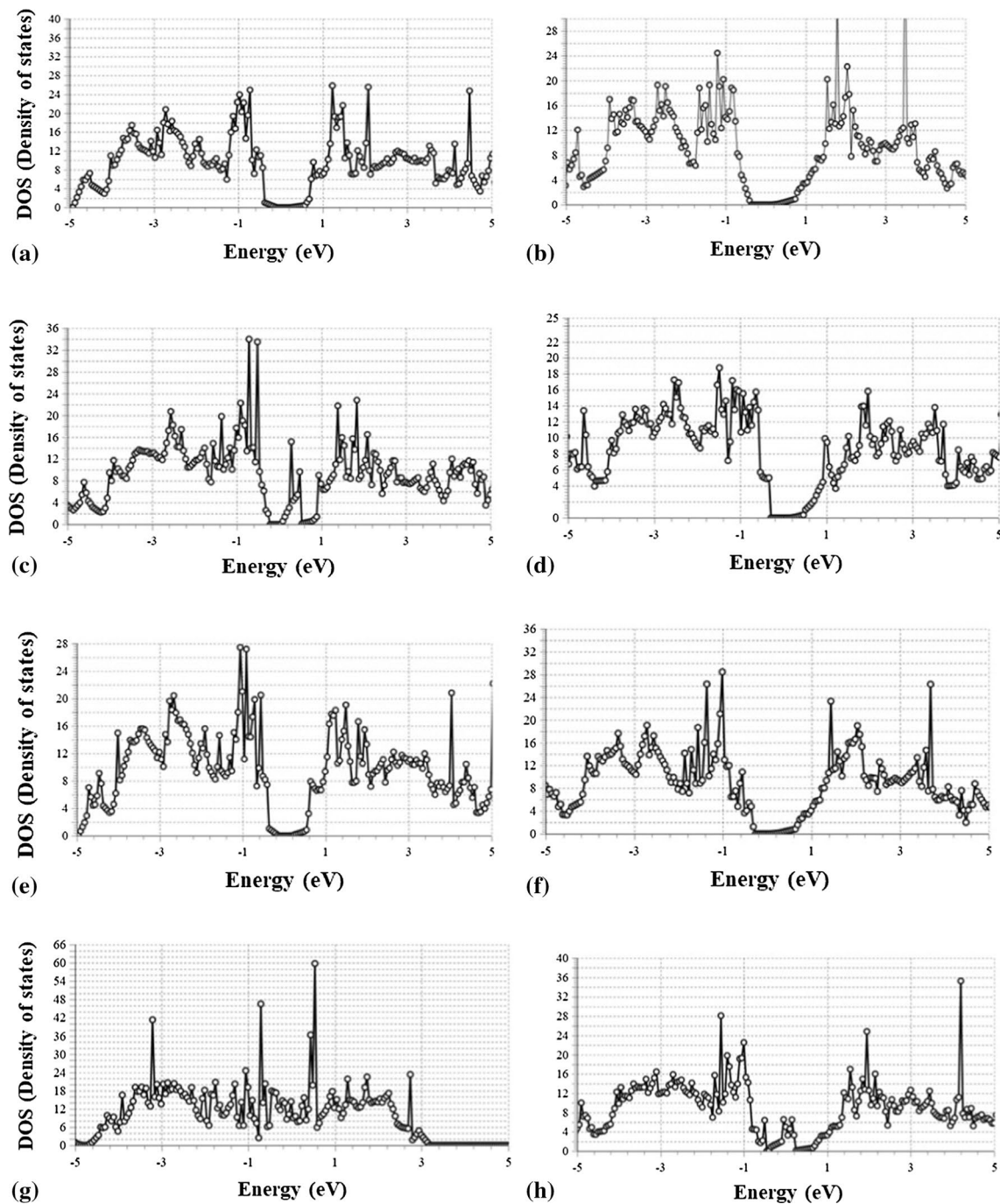
Fig. 18 Simulated density of states of (a) Bi_2Te_3, (b) Bi_2Se_3, (c) $(Bi_{1-x}In_x)_2Te_{2.7}Se_{0.3}$, (d) $(Bi_{1-x}In_x)_2Se_{2.7}Te_{0.3}$, (e) $(Bi_{1-x}Sb_{1x})_2Te_{2.7}Se_{0.3}$, (f) $(Bi_{1-x}Sb_x)_2Se_{2.7}Te_{0.3}$, (g) $(Bi_{1-x}Sn_x)_2Te_{2.7}Se_{0.3}$, and (h) $(Bi_{1-x}Sn_x)_2Se_{2.7}Te_{0.3}$.

Use of Bi_2Te_3 and Bi_2Se_3 Material as a Device

The thermoelectric properties of bismuth chalcogenides were verified by Thomas Seebeck in 1822–1823 with the common Palestine minerals Bi_4Te_3 and Bi_2Se_3. The Bi–Te binary system was found to possess a large Seebeck coefficient. The Bi-Te/Se binary is classified into p and n types based on whether it is prepared using Bi-rich or Te composition.[187] When there was an availability of both n-type and p-type Bi_2Te_3, greater cooling of 40°C was attained in 1955[188] and was again increased to 65°C by Sheard et al.[189] The optimization of thermoelectric properties of bismuth chalcogenides was carried out by Loffe et al.[190] Optimized alloys Bi_2Te_3–Bi_2Se_3 and Bi_2Te_3–Sb_2Te_3 having

very low thermal conductivity were prepared for device fabrication.[40,191,192] The most suitable single-stage Peltier cooler based on the compound Bi_2Te_3/Se_3 shows the generation of maximum potential differences at temperatures of 75 K and 300 K for the cold and hot sides, respectively.[193] In contrast, multistage coolers have observed higher differences by evading compatibility factors.[194] By regulating the carrier concentration, the temperature difference can be increased by 9%.[195] The Carnot efficiency of commercially available power modules is about 13%.[196] As the power generator operates at elevated temperatures, there is a suppression of the bipolar effect. Hence, doping, alloying, and material processing are vital in improving the device quality of bismuth chalcogenides at a desired temperature.[197]

Table II Fermi energies of pristine and In/Sb/Sn-doped Bi_2Te_3 and Bi_2Se_3 compounds

S. no.	Compound	Fermi energy (eV)
1	Bi_2Te_3	7.0726
2	Bi_2Se_3	6.7959
3	$(Bi_{1-x}In_x)_2Te_{2.7}Se_{0.3}$	6.5452
4	$(Bi_{1-x}In_x)_2Se_{2.7}Te_{0.3}$	6.7269
5	$(Bi_{1-x}Sb_{1x})_2Te_{2.7}Se_{0.3}$	6.5807
6	$(Bi_{1-x}Sb_x)_2Se_{2.7}Te_{0.3}$	6.7011
7	$(Bi_{1-x}Sn_x)_2Te_{2.7}Se_{0.3}$	6.4802
8	$(Bi_{1-x}Sn_x)_2Se_{2.7}Te_{0.3}$	6.3002

Thermoelectric Wearable Devices

Metabolic heat dissipation such as that occurring during running or walking is a valuable source of thermoelectric energy production. Harvesting of the energy is accomplished by transducers to generate electric power for domestic devices. For the comfort, robustness, and inter-device communication of all users, the design, fabrication, and evaluation of self-powered monitoring in enhanced wearable instruments have been sponsored by the National Science Foundation (NSF) since 2012.[198] In 1998, the first commercial thermoelectric wristwatch was developed with 300 mV of open-circuit voltage, 0.1% efficiency conversion, and 25 µW output power over a temperature difference of 1.5°C.[199] Though wearable thermoelectric generators cannot offer sufficient power for more sophisticated power electronics, they can power lower-energy wearables. Using the heat from a more significant part of the body, the power can be enhanced. The significant advances in thermoelectric wristwatches were related to the TEGs, power organization, and heat transfer design.

To increase the power output of TEG instruments, attentive inspection is supposed to be given for the design of TEG instruments.[200,201] The factors consist of load-matching heat spreaders, filler material, and interconnection of metals and substrates.[202–205] The lateral heat lost through fillers reduces the temperature gradient and degrades the output power of the TEG.[206] For an instrument with a 10% fill factor of 0.3 W/mK thermal conductivity and 0.03 W/mK filler conductivity, there is equilibrium between the total thermal conductivity of the thermoelectric material and the filler. Thus,
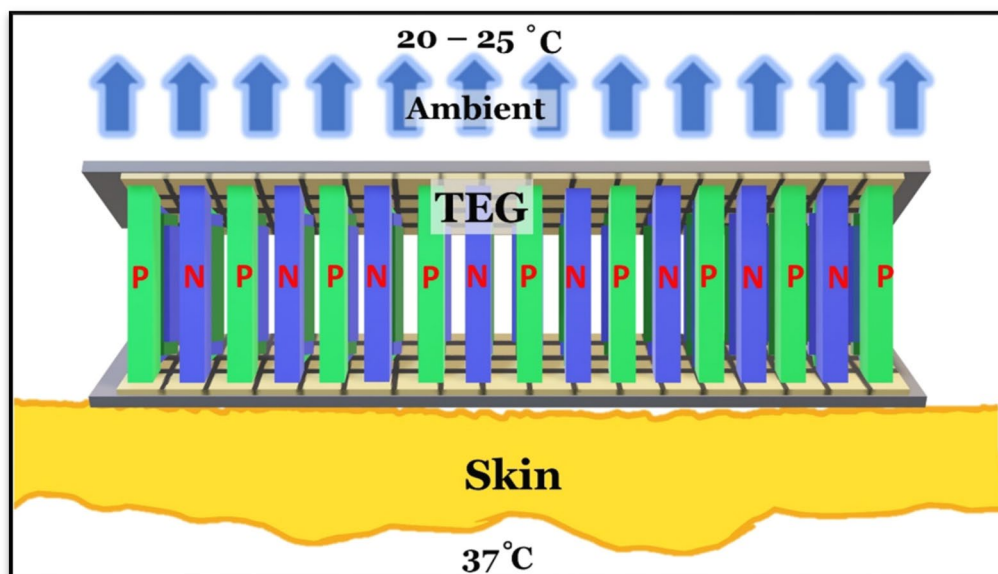
Fig. 19 Schematic view of a TEG for body heat harvesting.

half of the heat is drained by the conduction in decreasing the output power.

Generally, a metal electrical interconnection is mounted on an insulating ceramic substrate (Fig. 19). These metal interconnections possess high electrical conductivity and corresponding thermal expansion, where they are made of gold-coated copper of thickness 20 μm.[207] If TEG leg resistance is comparable to the contact of resistance, the interfacial resistance between the TEG legs and interconnections can bound the instrument performance. This phenomenon is possible only when contact resistance surpasses 10% of $\frac{\rho L}{2}$ where ρ is electrical resistivity and L is the length of the TEG. The ρ of 10^{-3} Ω cm and contact resistance of 10^{-3} Ω cm^2, and a leg length of more than 0.2 mm are the ideal factors for the TEG.[208] The interconnects in unbending TEGs are characteristically attached to a highly thermally conductive substrate of alumina ceramics.[209] The parasitic series thermal resistance is less than the resistance detected from the TEG. The resistance of the TEG can be increased by reducing the fill factor, which can be accomplished by decreasing the number of n- and p-type legs, increasing the aspect ratio of the legs, or decreasing the thermal conductivity of the legs.

TEG performance is limited by the skin–TEG interface and TEG–ambient interface. Human skin is called a thermal insulator, which creates the resistance between the core of a TEG and the body. The surface roughness of the skin is the reason for the contact resistance between the interface of the skin and TEG. The air–TEG interface resistance is frequently used if no heat sink is utilized on the upper part of the TEG. The contact pressure and the characteristics of the skin influentially modify this thermal resistance.[183,210] When the TEG is situated on body skin, the maximum power generated from a TEG decreases by 30%.[211,212]

Heat spreaders improve wearable TEG performance. The light weight and the flexibility are advantages of a heat spreader over a fin heat sink required for wearable applications. To improve the output power of the TEG hot and cold sides, heat spreaders are placed on either side of the TEG. To maximize the power generation, copper and carbon foils need to have 1000 W/mK and 400 W/mK of thermal conductivity and 100 μm and 250 μm of thickness, respectively.[213] Broadening the surface area of a spreader increases the power output up to a strong point, and the lateral thermal resistance is initiated to control the spreader role, which becomes less significant. The output power was amplified by 100% using a spreader of 16 mm^2, which is very high compared to a TEG without a heat spreader. The temperature gradient and thermal resistance are found to reduce by increasing the number of TEG legs. For a human body TEG, the maximum temperature gradient is found to be less than 2°C with a fill factor of 10%.[214] The output power increases by increasing the aspect ratio, modifying the leg shape, and

lowering the fill factor across the module.[210,211] If a module has a fill factor in the range of 0.3% to 3%, it generates more power per unit area compared to instruments with a fill factor of more than 25%, whereas a module having a fill factor of less than 20% could compromise the integrity of mechanics.[215–217] The challenging process is TEG instrument fabrication and optimization of instrument parameters to boost converter output. Energy generation in a TEG is directly dependent on lowering the contact resistance of the module legs and maximization of the module steadiness in different environments.

Future Challenges

By the end of 2022, the worldwide market for wearable technologies is predicted to exceed $78 billion. The effectual body energy harvester unlocks the possibility of battery-less electronics of wearables to care for human health and ecological conditions. The wellness of health and user comfort will be monitored through thermoelectric watches, headbands, cuffs, innovative jewelry, and textiles. This digital and mobile health promises a reformed arrangement and distribution of medical care to authorize health teams to support patient monitoring and repossession. However, the output power levels are still low for practical applications, regardless of the effort to incorporate TEGs in textiles. Current TEGs have not been developed as thermoelectric instruments in materials science with the unparalleled efficiency of thermoelectricity.

Conclusion

The review and summary of different processing aspects and their impact on thermoelectric properties of doped/composite bismuth chalcogenide materials have been discussed in this article. It is recognized that an appropriately doped and composite structure generally leads to enhanced thermoelectric performance. Mechanical alloying and high-energy ball milling are appropriate methods utilized in research laboratories and are easily scaled up in industries. In some cases, the development of compositional homogeneity can be obtained by melting/pulverizing processes carried out using ball milling for the resultant extracts. The soft chemical reaction method is employed to synthesize nanoparticles with controllable size and surface morphological features. To lower the sintering temperature with less time, spark plasma sintering is performed for bulk polycrystalline materials. SPS can also overturn the grain growth through rapid heating and low-temperature sintering, which is very prominent in retaining the morphology. Remarkably, the solid-state reaction consolidated sintering is also used to create a polycrystalline structure. In general, thermoelectric

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