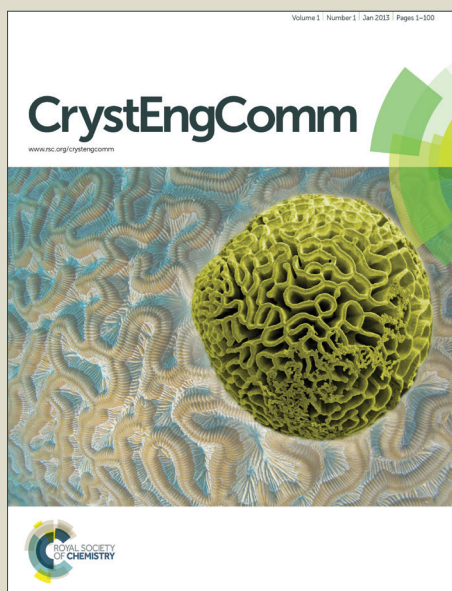


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## ARTICLE

## Tailoring the bismuth telluride nanostructures by a scalable sintering process and its thermoelectric properties

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Bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) nanocrystals were synthesized by wet chemical method and 1 mm thick pellets of nanocrystals were made with 10 mm diameter by high pressure and high temperature sintering (HPHTS) process. The nanostructures were tailored by sintering process and the impact of sintering temperature on morphological evolutions and phase transformation of pelletized  $\text{Bi}_2\text{Te}_3$  nanocrystals were studied by standard analytical techniques. The phase change was observed from  $\text{Bi}_2\text{Te}_3$  to  $\text{BiTe}$  in the pellets sintered at high temperatures and  $\text{BiTe}$  phase was dominated in the 773 K sintered pellets. Thermoelectric properties of as-prepared and sintered pellets were measured. Seebeck coefficient of  $\text{Bi}_2\text{Te}_3$  nanocrystals was increased with sintering temperature and reasonably decreased at higher sintering temperature (>673 K). Moreover, the power factor of sintered  $\text{Bi}_2\text{Te}_3$  nanocrystals was significantly enhanced. The variations of Seebeck coefficient and power factor is explained by a proposed model using the phase and morphological changes in the sintered  $\text{Bi}_2\text{Te}_3$  pellets.

### Introduction

Recently, increasing global warming due to  $\text{CO}_2$  emission from all over the world stimulated the search for alternate way of generating electricity instead of the burning of fossil fuel. Thermoelectric (TE) energy conversion is one of the promising ways to convert the waste heat into electric energy. The performance of thermoelectric energy conversion devices depends on the value of dimensionless figure of merit (ZT) which is given as

$$ZT = S^2 \sigma T / \kappa \quad (1)$$

where,  $S$  is the Seebeck coefficient,  $\sigma$  is electrical conductivity,  $T$  is the temperature and  $\kappa$  is the total thermal conductivity.<sup>1,2</sup> The overall efficiency of a TE cell depends on the ZT value of the TE materials. Enormous efforts have been made to enhance the ZT, such as forming thin films of TE materials,<sup>3-7</sup> synthesizing new composite materials by using different elements, incorporating nanograins in bulk material and making low dimensional nanomaterials with large number of grain boundaries and so on.<sup>8-12</sup> In the aforesaid approaches, making TE nanomaterials are expected as an efficient approach to enhance ZT values due to quantum confinement effect and increased phonon scattering at grain boundaries.<sup>13,14</sup>

Bismuth telluride is a well-known low temperature TE material and commercially available for practical applications. However, preparation of bulk material in large scale by conventional process such as directional crystallization is quite complicated as it needs sophisticated systems due to volatile nature and high vapour pressure of tellurium.<sup>15</sup> Moreover, as per the Bi-Te phase diagram, the compound has several other phases such as  $\text{BiTe}$ ,  $\text{Bi}_4\text{Te}_3$  and  $\text{Bi}_3\text{Te}_4$  and they were referred as bismuth telluride alloys (BTA). All the BTA structures have similar layered structures with hexagonal symmetry and larger c-axis lattice constants.<sup>16,17</sup> The effect of mixed BTA phases on the TE properties was rarely investigated.<sup>17</sup>

In nanomaterials, increasing phonon scattering at grain boundaries can reasonably control the thermal conductivity. At the same time,

electron transport may be degraded due to recombination at the charged defects and grain boundaries. Due to this fact, despite of better ZT, the power factor is relatively low for the nano TE material compared to its bulk counterpart.<sup>13</sup> Therefore, it is highly imperative to reduce the thermal conductivity and enhance the power factor to improve the ZT of nano TE material.

In the present work,  $\text{Bi}_2\text{Te}_3$  nanocrystals were synthesized by low temperature wet chemical synthesis method. The synthesized materials were made as pellets by high pressure and high temperature sintering (HPHTS) process. The sintering temperature was varied for making the materials with mixed nano and meso grains as the former favors the phonon scattering and later favors the electron transport. In addition, the phase transformation from  $\text{Bi}_2\text{Te}_3$  to  $\text{BiTe}$  was observed in the high temperature sintered pellets. The effect of mixed phases and nanostructures of  $\text{Bi}_2\text{Te}_3$  on the TE properties was investigated. The power factor of the  $\text{BiTe}$  nano and micro structure was enhanced up to one order compared to reported values for  $\text{BiTe}$  nano structures.

### Experimental

#### Synthesis

20 mmol Bismuth chloride ( $\text{BiCl}_3$ ), 30 mmol Tellurium chloride ( $\text{TeCl}_4$ ) and 2 gm of ethylenediaminetetraacetic disodium salt ( $\text{EDTA} \cdot 2\text{Na}$ ) were taken in a 1000 mL beaker with 500 mL of 343 K preheated deionized water. 3.5 gm of sodium hydroxide ( $\text{NaOH}$ ) and the same amount of sodium borohydride ( $\text{NaBH}_4$ ) were added as reducing agents and stirred by a magnetic stirrer at 343 K. The solution was continuously stirred for 12 h at the same temperature and allowed to cool without stirring. The synthesized grey coloured powder was dried in a hot air oven below 343 K for 6 h. Pellets were made with 1 mm thickness and 10 mm diameter by HPHTS process under the optimized pressure at room temperature. The

pellets were sintered at 573, 673 and 773 K at flowing Ar<sup>+</sup> atmosphere for 1 h to study the effect of sintering temperature on the structural, morphology and thermoelectric properties.

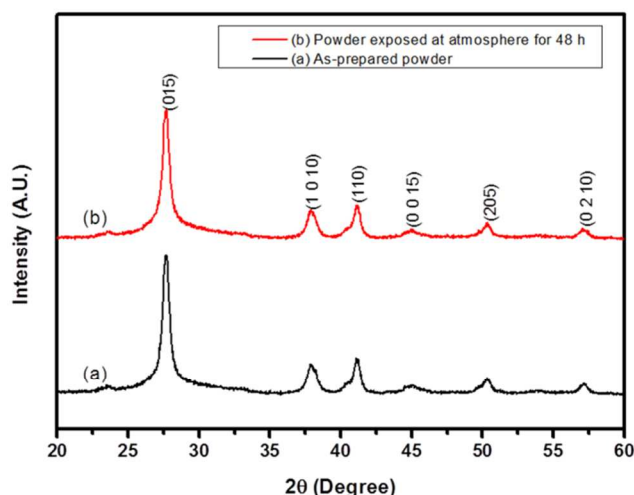
### Characterization

The samples collected from as-prepared, and sintered pellets were subjected to X-ray powder diffraction (XRD) analysis. The XRD patterns were recorded over the  $2\theta$  range between 20 and 60° by Rigaku X-ray diffractometer with CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The compositions of the samples were analyzed by energy dispersive spectroscopy (EDS). JEOL 7001F field emission scanning electron microscope (FESEM) equipped with EDS and JEM 2100F transmission electron microscope (TEM) were used to analyze the chemical composition and nanostructures of the material. X-ray photoelectron spectroscopy (XPS) analysis was performed using Shimadzu ESCA 3400 electron spectrophotometer. The electrical conductivity of the samples was measured by Hall measurement system. Seebeck coefficient was measured at room temperature by using an in-house made high precision instrument, in which, the thermo emf and temperature differences were recorded by Keithley 2700 multimeter. For the sample sintered at 673 K, the Seebeck coefficient was measured as a function of temperature.

## Results and Discussion

### Structural analyses

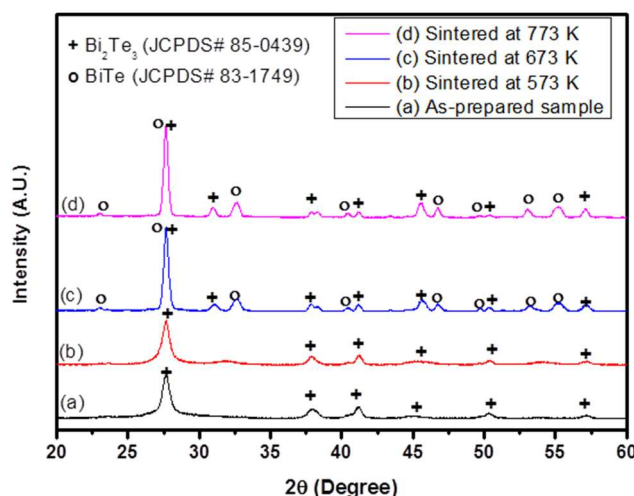
XRD pattern of the as-prepared sample is shown in Fig.1. The synthesized sample was confirmed as Bi<sub>2</sub>Te<sub>3</sub> by comparing the recorded diffraction pattern with the standard powder diffraction data of JCPDS # 85-0439 (ICSD code 15753). To analyze the stability of the synthesized sample, the XRD for the sample exposed to open atmosphere for 48 h was recorded (Fig. 1b) and the pattern was similar to that of as-prepared (Fig. 1a) sample. From the results, it was confirmed that the sample was stable at least for 48 h with no detectable oxide formation. Therefore it was confirmed that the Bi<sub>2</sub>Te<sub>3</sub> was synthesized as a single phase by the simple wet chemical method.



**Fig. 1** Powder X-ray diffraction patterns for (a) as-prepared samples (b) samples exposed to atmosphere for 48 hours.

Fig. 2 a-d shows the XRD spectra of as-prepared and sintered pellets samples. From the spectra, it is obvious that the Bi<sub>2</sub>Te<sub>3</sub> phase was stable until the sintering temperature of 573 K and BiTe phase

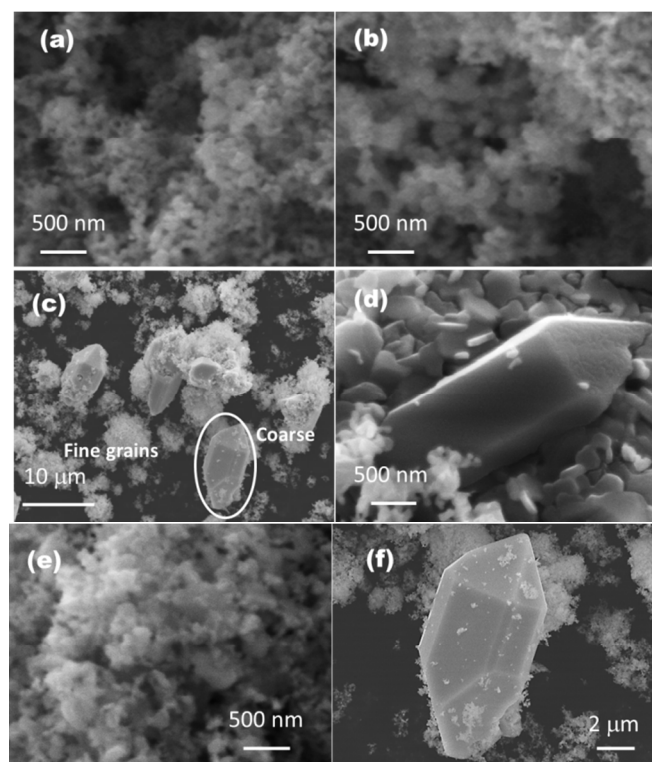
was formed in addition with Bi<sub>2</sub>Te<sub>3</sub> in the sample sintered at 673 K (Fig.2c). Moreover, the BiTe phase was dominated in the sample sintered at 773 K as the number of BiTe related diffraction peaks were increased in Fig. 2d. From the Fig.2, it is clear that the sintering temperature effectively influenced on the mixed phase formation and crystallization process in the samples as the intensity of the prominent peak increased with sintering temperature. Tellurium may be vaporized at high sintering temperature due to its high vapor pressure ( $2 \times 10^{-2} \text{ mmHg}$ ) compared to bismuth ( $7 \times 10^{-7} \text{ mmHg}$ ) (at 673 K), and hence the tellurium may be insufficient to form Bi<sub>2</sub>Te<sub>3</sub> which resulted the formation of BiTe.<sup>18</sup>



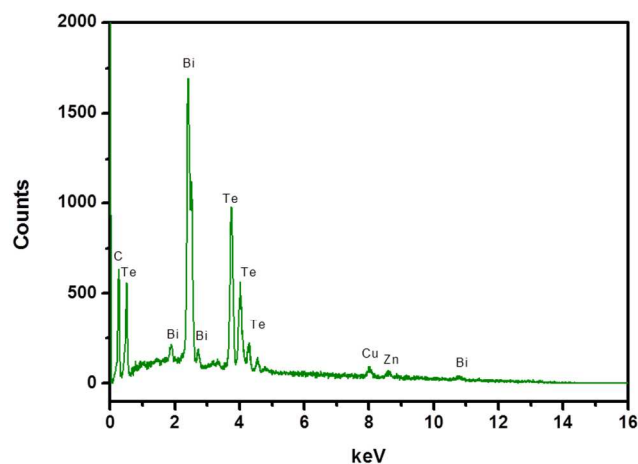
**Fig. 2** Powder X-ray diffraction patterns for (a) as-prepared samples and sintered samples at (b) 573 K (c) 673 K and (d) 773 K.

### Morphological and compositional analyses

FESEM images of as-prepared and sintered samples are shown in Figs.3 a-f. Crystallization of the samples during the sintering process is clearly illustrated in the FESEM images (Figs. 3 a-d). As can be seen from Fig. 3a, the as-prepared samples were nearly spherical with mono dispersion probably due to the effective passivation of the nanocrystals by EDTA, which was added during synthesis process. The morphology and size of the 573 K sintered sample (Fig. 3b) was quite similar to the as-prepared sample. From the Fig. 3c, it is obvious that the material started to grow and thus micro crystals were observed in between the nanocrystals at 673 K. Moreover, the sizes of the nanocrystals were increased up to 100 nm along with larger micro crystals (Fig. 3c). Subsequently, the material contained the mixture of micro and nano crystals (hereafter it is called as coarse and fine grains).<sup>2</sup> On the other hand, in the materials sintered at 773 K, the nano crystalline particles were grown reasonably and the sizes were in the range of 400-700 nm as shown in Fig. 3-d. Whereas, the size of the micro crystals were quite similar to the sample sintered at 673 K possibly due to the growth of nano crystals. Figs 3 e and f are the magnified images of fine grains and coarse structures, respectively. Figure 4 shows the EDS spectrum of the as-prepared sample and the composition data of all the samples were tabulated in table 1. As can be seen from table 1, the composition of as-prepared and 573 K sintered sample shows the Bi<sub>2</sub>Te<sub>3</sub> phase, as it is highly stable at low temperature<sup>19</sup>. Whereas the tellurium deficient was observed in the high temperature (>573 K) sintered samples and thereby BiTe phase was formed<sup>19, 20</sup>. The tellurium deficient is probably due to its evaporation as the tellurium is lighter and more volatile than Bi<sup>21, 22</sup>.



**Fig. 3** FESEM images of (a) as-prepared (b) sintered at 573 K (c) 673 K, (d) 773 K (e) magnified image of fine grains and (f) coarse structure at 773 K

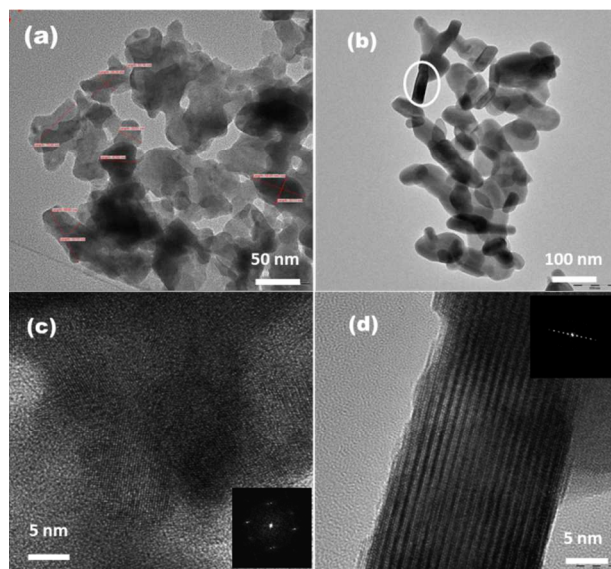


**Fig. 4** Energy dispersive x-ray spectrum of as-prepared sample

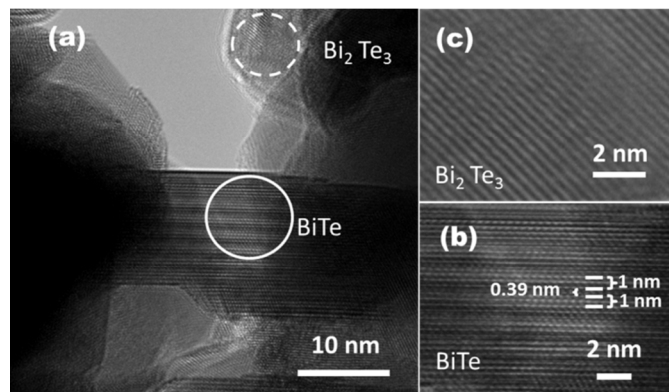
**Table 1** EDS data for as-prepared and sintered samples

| Sample Powder | Atomic Percentage |       | Weight Percentage |       | Composition              |
|---------------|-------------------|-------|-------------------|-------|--------------------------|
|               | Bi                | Te    | Bi                | Te    |                          |
| As prepared   | 42.84             | 57.16 | 51.23             | 48.77 | $\text{Bi}_2\text{Te}_3$ |
| 573 K         | 45.07             | 54.93 | 53.26             | 46.74 | $\text{Bi}_4\text{Te}_5$ |
| 673 K         | 55.56             | 44.44 | 63.19             | 36.81 | $\text{BiTe}$            |
| 773 K         | 56.47             | 43.53 | 63.05             | 36.95 | $\text{BiTe}$            |

Figs. 5 a-d show the TEM and HRTEM images of as-prepared and 673 K sintered samples. As shown in Fig. 5a, as-prepared samples have nanocrystals with sizes ranging from 20-70 nm. Lattice fringes of particles were observed as shown in HRTEM image (Fig. 5c) and the corresponding FFT pattern shown in the inset of Fig. 5c shows the good crystalline nature of the as-prepared samples. The nanocrystals were grown with preferred orientations in the 673 K samples as the shape changed from spherical to rod like structure (Fig. 5b). One of the rod marked as white circle in Fig. 5b is shown in Fig. 5d with high magnification. The width of the crystal was measured to be 25 nm and the length around 100 nm. It was clearly observed that the sizes of the crystals and crystallinity were significantly increased during the sintering process. Fig. 6a shows the HRTEM image of sample sintered at 673 K. From the image, two different stacking of the material was clearly observed as encircled with continuous and dotted lines. The BTA alloy materials have the layered structure in the sequence of Te-Bi-Te-Bi-Te with the thickness of 1 nm and stack along c-axis by Van der Waals forces<sup>23</sup>. The  $\text{BiTe}$  has the Bi-Bi layer of 0.39 nm between two 1 nm thin 5-layer structures<sup>17</sup> as it was observed in Fig. 6b. The other type of lattice fringes without layer structures is also observed in Fig. 6c, which corresponds to  $\text{Bi}_2\text{Te}_3$  phase. From the image, one can observe that the sample contains both phase of  $\text{BiTe}$  and  $\text{Bi}_2\text{Te}_3$ .

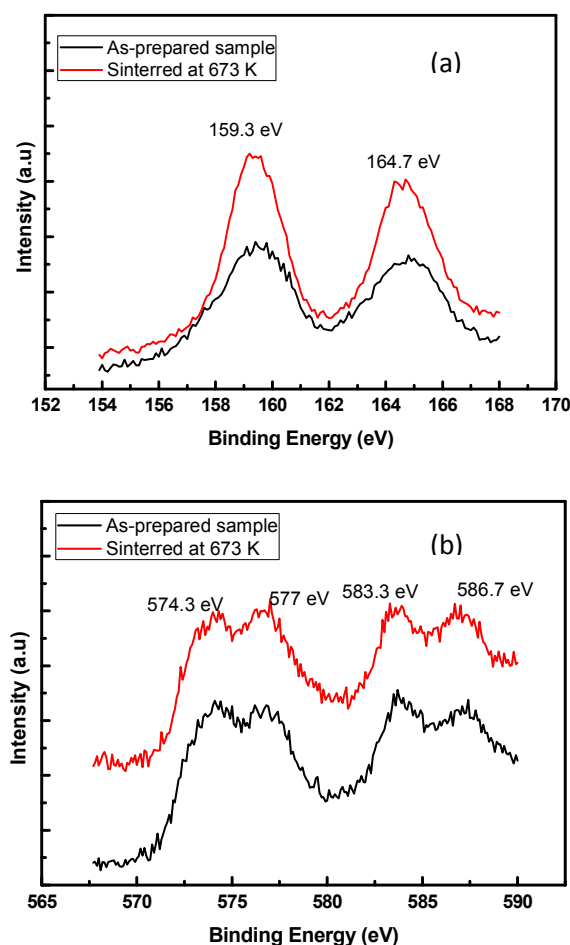


**Fig. 5** TEM and HRTEM images of (a) & (c) as-prepared (b) & (d) sintered at 673 K, respectively.



**Fig. 6** HRTEM images of (a) sample sintered at 773 K, (b) & (c) show the lattice fringes of  $\text{BiTe}$  and  $\text{Bi}_2\text{Te}_3$  respectively.

Figure 7 a and b shows the core level XPS signals of Bi and Te for the as prepared and 673 K sintered samples. The two distinct peaks at 159.4 and 164.8 eV (Fig.7a) correspond to the binding energies of Bi 4f<sub>7/2</sub> and Bi 4f<sub>5/2</sub> of Bi<sub>2</sub>Te<sub>3</sub>, which are well agreed with the reported values. Moreover, the XPS spectra for Te (Fig.7b) show the doublet peaks at 574.3 and 583.3 eV, which correspond to the reported binding energies of Te 3d<sub>5/2</sub> and Te 3d<sub>3/2</sub> of Bi<sub>2</sub>Te<sub>3</sub> respectively. Furthermore, the two peaks at 577 and 586.7 eV in the Te 3d region (Fig.7b) represents the oxidized state of Te as the binding energies are matching with TeO<sub>2</sub>. Whereas, in the Bi spectra, no peaks related to oxidation state of Bi was observed. The Te oxidation is possibly occurred during the pelleting the sample as it was observed both in as prepared and sintered samples. As can be seen from Fig. 7a, the intensity of Bi peaks is quite high for the sintered sample. It seems that the surface of sintered sample is Bi richer. From the quantitative analyses of the XPS spectra, the as-prepared sample has 42.36 and 57.64 at % of bismuth and tellurium respectively. While, the sample annealed at 673 K had 53.25 and 46.74 at % of bismuth and tellurium, which confirms the phase transformation from changes from Bi<sub>2</sub>Te<sub>3</sub> to BiTe as evidenced from the EDS and XRD analysis.

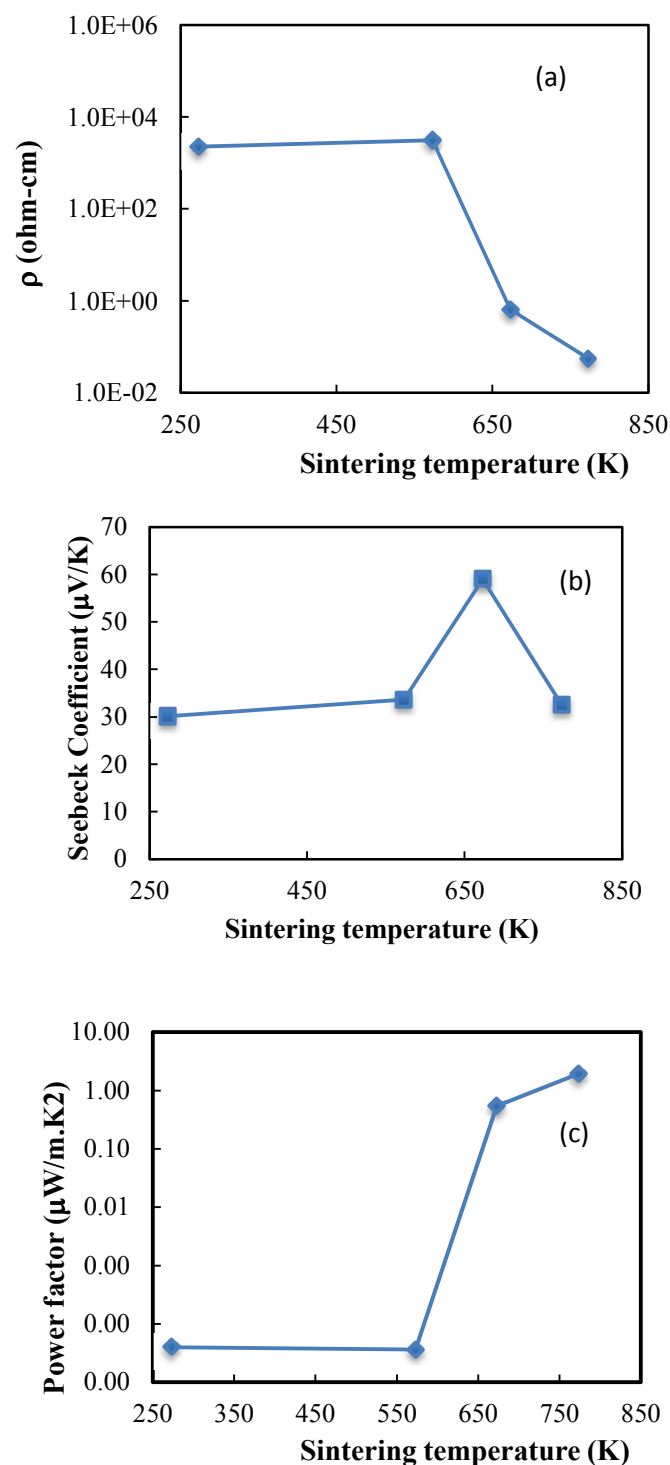


**Figure 7:** XPS spectra for (a) Bi 4f and (b) Te 5d of as prepared and 673 K sintered Bi<sub>2</sub>Te<sub>3</sub> samples.

### Thermoelectric properties

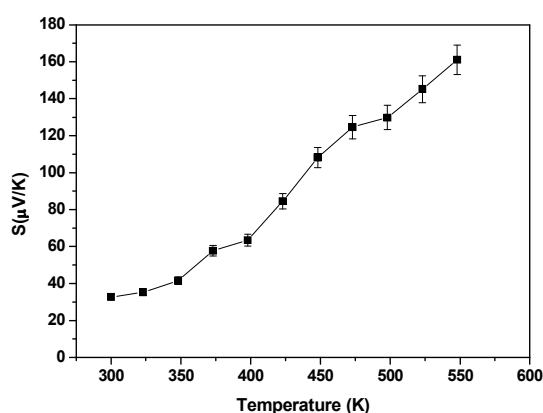
The resistivity of the as-prepared and sintered samples was measured at room temperature by Hall measurement system. Figure 8a shows

the variation of electrical conductivity as a function of sintering temperature. The electrical conductivity of the samples was very low for the as-prepared Bi<sub>2</sub>Te<sub>3</sub> sample. There was no significant change of conductivity in the low temperature (573 K) sintered sample. Whereas the conductivity increased drastically as the sintering temperature increased beyond 573 K.



**Figure 8:** Variation of (a) electrical resistivity and (b) Seebeck coefficient and (c) power factor of Bi<sub>2</sub>Te<sub>3</sub> with sintering temperature.

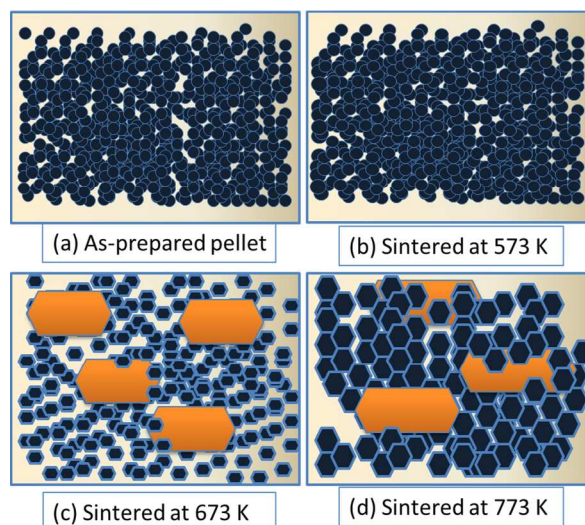
The variation of Seebeck coefficient as a function of sintering temperature is shown in Fig. 8b. The Seebeck coefficient of the sample increased with sintering temperature with highest Seebeck coefficient of  $59 \mu\text{V/K}$  for the sample sintered at 673 K. Whereas, the Seebeck coefficient of 773 K sintered sample decreased to  $32.6 \mu\text{V/K}$ . The small Seebeck coefficient at high temperature (773 K) sintered sample is possibly due to high electrical conductivity of the sample. The power factor ( $\alpha^2\sigma$ ) was calculated from the measured electrical resistivity ( $\rho$ ) and Seebeck coefficient ( $\alpha$ ). The calculated power factor was plotted as a function of sintering temperature (Fig. 8c). The power factor was increased drastically when the sintering temperature increased above 573 K. Moreover, the Seebeck coefficient of the 673 K sintered sample was measured at various temperatures (300 to 573 K) under Ar atmosphere using a specially



**Fig. 9** Seebeck coefficient of 673 K sintered  $\text{Bi}_2\text{Te}_3$  sample as a function of temperature.

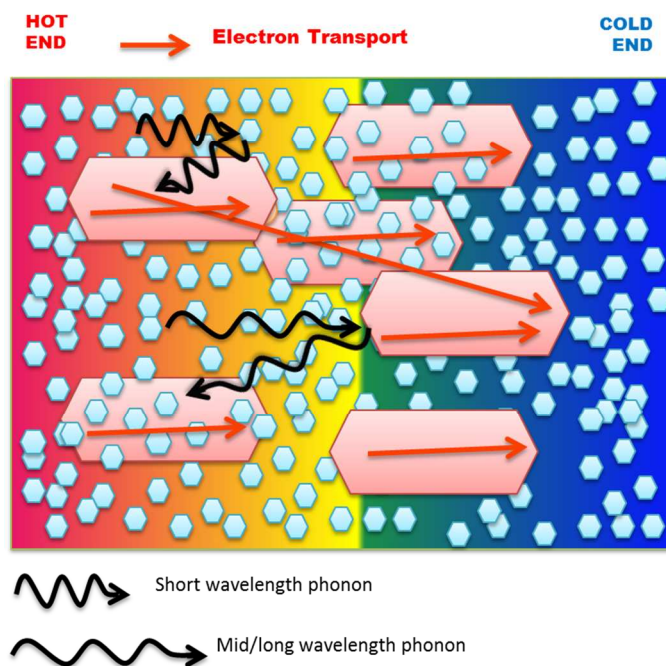
designed system. The Seebeck coefficient increased with temperature from 31 to  $161 \mu\text{V/K}$  as shown in Fig. 9.

The morphological changes, which are observed in the TEM and FESEM analysis, were schematically shown in Fig. 10. The as synthesized nanocrystals (Fig. 10 a) are mono dispersed with no agglomerations as confirmed by FESEM and TEM analysis. The sample sintered at 573 K (Fig. 10b) retains the same nanostructures, as the materials are not agglomerated. However, when the sintering temperature increases from 573 K to 673 K, the material started to agglomerate and coarse structures (indicated as large size hexagonal in Fig. 10c) are formed through the complicity of fine grains. In the sample sintered at 773 K (Fig. 10d) further growth was observed not only in the coarse structures but also in the fine grains. The disparity in the electrical conductivity, Seebeck coefficient and power factors can be explained using the model shown in Fig. 11. As shown in XRD and EDS analysis, the composition of the as-prepared sample is confirmed as  $\text{Bi}_2\text{Te}_3$  phase of BTA. The  $\text{Bi}_2\text{Te}_3$  phase of BTA is known to have high Seebeck coefficient when compared to other phases.<sup>24, 25</sup> In our experiments, the  $\text{Bi}_2\text{Te}_3$  material shows the Seebeck coefficient of  $30 \mu\text{V/K}$  which is comparatively lower than the reported value.<sup>24</sup> From the morphological analysis, the as-prepared sample contains the nanocrystals in the size of 20 to 70 nm which causes small Seebeck coefficient due to large number of grain boundaries when it was made as dense pellets. The morphology of the 573 K sintered sample has no significant change (Figs. 10 a & b) and thus there is no variation in the electrical conductivity and



**Fig. 10** Schematic representation of the morphological changes of  $\text{Bi}_2\text{Te}_3$  during sintering process.

Seebeck coefficient as well (Fig. 8a-c). The clear morphological changes are observed in the 673 K sintered sample as the sample becomes coarse and grains structures due to the sintering process (Fig. 10c).



**Fig. 11** A model to explain the disparity of electrical conductivity and Seebeck coefficient.

The formation of coarse structures favours the electron transport, as the number of grain boundaries was decreased due to the growth of micro size coarse structures as shown in Fig. 10. Electrons can transport ease in the coarse structures and through the electrically neutral grain boundaries unlike the phonon scattering, which enhance the electron transport in the fine and coarse structures. As a result, the TE characteristics were relatively enhanced at 673 K sintered samples. The power factor is relatively low for the as-prepared sample at room temperature whereas it is highly enhanced up to  $2 \mu\text{W}/\text{cmK}^2$  by sintering process. In the sample sintered at 773 K, the nanocrystals were grown larger in addition with the coarse structures as shown in Fig. 9d. It enhances the electron transport when compared to low temperature-sintered samples and thus drastic enhancement of electrical conductivity is observed. Moreover, the BiTe phase, which has high electrical conductivity,<sup>21</sup> were dominated in the sample sintered at 773 K as evidenced from the EDS and XRD analysis. Due to the high electrical conductivity, the Seebeck coefficient was slightly decreased possibly due to high electron-electron and electron-phonon scattering.<sup>13</sup> From the results, it is demonstrated that the mixed structures of coarse and grains are quite suitable for enhancing the power factor of the  $\text{Bi}_2\text{Te}_3$  material and HPHTS process is an appropriate approach to achieve such a structure.

## Conclusion

$\text{Bi}_2\text{Te}_3$  nanocrystals were synthesized by simple wet chemical method. The morphology of  $\text{Bi}_2\text{Te}_3$  nanocrystals were tailored by HPHTS process. From XRD analyses, it was found that the synthesized material was transformed from  $\text{Bi}_2\text{Te}_3$  to BiTe phase during the HPHTS process. Conductivity of the material was increased with sintering temperature as the crystallinity and coarse structure increased which enhanced the transport properties. The room temperature Seebeck coefficient ( $59 \mu\text{V}/\text{K}$ ) and power factor ( $2 \mu\text{W}/\text{cmK}^2$ ) were enhanced especially for high temperature HPHTS processed samples. The present results demonstrated that the HPHTS tailoring approach has the large potential to enhance the thermoelectric efficiency of  $\text{Bi}_2\text{Te}_3$  nanocrystals.

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## Notes

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The size and phase of bismuth telluride nanocrystals were tailored by sintering process for the enhancement of thermoelectric properties.

