A Quintuple-Layered Binary Chalcogenide Sb$_2$Te$_3$ Single Crystal and Its Transport Properties for Thermoelectric Applications

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ABSTRACT: The binary chalcogenide material Sb$_2$Te$_3$ was synthesized via the melting technique. The synthesized materials were converted to a single crystal through the Bridgman–Stockbarger technique. The phase purity and structural properties of the grown crystal were analyzed using powder X-ray diffraction and single-crystal X-ray diffraction measurements. X-ray photoemission spectroscopy reveals the local intermolecular bonding, changes in the stoichiometry, and the oxidation states of the elements present in the crystal. Transport properties like electrical resistivity, Seebeck coefficient, and thermal conductivity were measured. The power factor and figure of merit (ZT) of the grown crystal were calculated.

INTRODUCTION

Researchers focus on thermoelectric materials as the demand for alternative energy resources has been increasing these days. To be more precise, thermoelectric (TE) materials can play a major role in engineering and technology because these materials are capable of directly converting heat to power generation. Proficient TE crystals possess a high electrical conductivity, Seebeck coefficient, and ultralow thermal conductivity. The requirement for TE materials is that they should have increasing power factor and figure of merit and a low thermal conductivity. The dimensionless figure of merit is analyzed through the relation $ZT = \sigma S^2 T / K$, where $\sigma$, $S$, $T$, and $K$ = $k_e + k_l$ are the electrical conductivity, thermopower or Seebeck coefficient, operating temperature, and electronic and lattice thermal conductivity, respectively. Achieving reasonable efficiency in TE materials is a challenging task because of the interdependency of required properties (electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and thermal conductivity). For a TE material to have a high figure of merit, it should have a high power factor and low thermal conductivity. PbTe-based alloys, TAGS (Te-Ag-Ge-Sb), and Si-Ge alloys are employed for mid- and high-temperature power generation applications, and solid Bi$_2$Te$_3$ (n-type Bi$_2$(Te, Se)$_3$) and p-type (Bi, Sb)$_2$Te$_3$ solutions are useful in refrigeration applications. In addition, the figure of merit of bulk PbTe materials ranges from 0.8 to 1, for which the corresponding thermoelectric efficiency is obtained around 5 to 6%. If the figure of merit is more than 1%, it is more suitable for heat-to-power generation.

In recent years, binary chalcogenide (A$_2$B$_3$) materials exhibit excellent topological properties and thermoelectric properties. Numerous materials such as Bi$_2$Se$_3$, Bi$_2$Te$_3$, Sb$_2$Se$_3$, and Sb$_2$Te$_3$ derived from groups V and VI are more suitable for thermoelectric device fabrication. Especially, Sb$_2$Te$_3$ is a highly efficient material for various applications such as topological insulators, phase change memory, water splitting, thermoelectric power generation, etc. Specifically, structural defects (stacking faults, twin boundaries, and dislocations) enhance the thermoelectric as well as topological properties. The pressure-induced disorder of Sb$_2$Te$_3$ alloy was investigated and reported by Zhao et al. However, a bulk-sized and defect-free single crystal has been grown using a modified Bridgman–Stockbarger technique; in the present work, the grown single crystal has been characterized using various studies like single-crystal X-ray diffraction (SXRD), powder X-ray diffraction (PXRD), X-ray photoelectron spectroscopy, and laser flash, electrical resistivity, Seebeck coefficient, and Hall measurements.

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INSTRUMENTATION FOR CHARACTERIZATION

The synthesized polycrystalline ST was subjected to PXRD analysis to confirm the phase purity of the materials using a PANalytical Empyrean powder X-ray diffractometer. The unit cell parameter of the grown single crystal was obtained using a Bruker Kappa APEXII single-crystal X-ray diffractometer with Mo Kα (λ = 0.710 Å) radiation. An elemental analysis and elemental oxidation state of elements were confirmed through Kratos Axis Ultra X-ray photoelectron spectrometer with monochromatized Al Kα X-ray source.

The Seebeck coefficients and electrical resistivity of the grown ST crystals were analyzed using an ECOPIA-HMS 3000. The thermal conductivity and diffusivity of the ST crystal were analyzed by a NETZSCH LFA 447 NanoFlash apparatus with a crystal dimension of 10 × 10 × 2 mm³. The Hall measurement of the ST crystal was performed using an ECOPIA-HMS 3000-type Hall measurement apparatus in the Van der Pauw configuration at room temperature, and 1 mm-thick wafer was used for this measurement with various temperatures.

RESULTS AND DISCUSSION

The PXRD pattern and refinement pattern of the synthesized ST polycrystalline material are shown in Figure 1a. All the peak positions of the compound exactly match with JCPDS card #15-0874. There is no secondary phase peak observed in the spectrum. The title material crystallizes in the rhombohedral crystal system with the space group R-3m (166). The unit cell dimensions of the ST single crystal obtained through refinement are a = b = 4.262 Å, c = 30.450 Å, and V = 479.01 Å³. All the diffraction peaks are sharp and strong, which indicates that the synthesized material is of good crystalline nature. All the diffraction planes were indexed. The refined crystallographic parameters of the ST crystal are given in Table 1.

The grown ST single crystals were investigated for their structural properties using SXRD. The obtained unit cell parameters of ST are a = b = 4.264 (3) Å, c = 30.452(9) Å, and V = 479.01 Å³, and the crystal system is rhombohedral. Also, these values are well matched with PXRD results. The results indicate that there is no secondary phase formed in the grown single crystal. Figure 1b displays the crystallographic structure of the ST single crystal. The experimentally obtained cell parameters of the ST crystal match well with the JCPDS card and refined unit cell parameters.

The ST crystal is composed of quintuple layers (QLs) in a rhombohedral system. QLs contain five monoatomic planes in the order of Te₁-Sb-Te₂-Sb-Te₁. Nearby QLs are bonded with van der Waals forces; moreover, the atoms in the QLs are bonded with covalent bonds. The chemical composition and the individual element oxidative states were elucidated through XPS studies. The XPS survey spectrum of the ST single crystal is shown in Figure 2a. Here, the individual element oxidative state spectra were normalized, viz., C 1s (285 eV) as a standard peak. Carbon correction has been made in the survey and core-level spectra. The carried carbon correction value is 0.8 eV. Figure 2b shows the 3d core-level spectrum of the Sb element.

| parameter         | ST crystal          |
|-------------------|---------------------|
| crystal system    | rhombohedral        |
| space group       | R-3m (166)          |
| a, b, c (Å)       | 4.267, 4.267, 30.455|
| α, β, γ (°)       | 90, 90, 120         |
| V (Å³)            | 479.01              |
| Rwp               | 11.7                |
| Rp                | 8.13                |
| Rwp               | 10.6                |
| χ²                | 1.21                |

Table 1. Refined Crystallographic Parameters of the ST Crystal

Figure 1. (a) PXRD patterns of Sb₂Te₃; (b) systematic crystal structure of the ST single crystal.
peak separation value is 8.8 eV, and the appearance of an additional satellite peak in the core spectra is due to the oxygen–antimony interaction. Further, the binding energy region of Sb 3d is overlapped with the O 1s binding energy state. In addition, Figure 2c shows the 3d core-level spectrum of the Te element. The peak separation between 3d_{3/2} and 3d_{5/2} is 10.4 eV. The additional satellite peaks in the Te 3d core spectra denote the oxygen interaction with the Te element. The oxygen presence in the elements was unavoidable due to the experimental conditions. The bonding of elements with oxygen may happen due to the melt contact with a growth ampoule. The growth ampoule was made up of SiO₂ (quartz), and the subjected wafer was taken out very close to the periphery from the grown crystal.

To measure the electrical properties, the ST crystal has been crushed into fine powder and pressed as rectangular pellets with a dimension of 16 × 5 × 3 mm³. The pellet is sintered at 250 °C under an argon atmosphere for further measurements. The electrical properties of the ST were measured in the range from 30 to 200 °C. The resistivity of the material is decreasing monotonically as a function of temperature, revealing the semiconductor nature of the grown crystal. This process could be explained in such a way that semiconductors behave like an insulator at low temperatures, i.e., the electrons are trapped within the atom. As the temperature of the semiconducting material is increased, the electrons in the valence band gain sufficient energy to escape from the confines of their atoms. Hence, at higher temperatures, resistivity decreases as valence electrons are set free, resulting in the conduction of the material. The electrical resistivity of the ST is shown in Figure 3. Generally, the electrical resistivity was calculated from expression 1

\[
\rho = \frac{RA}{l}
\]

where \( \rho \), \( R \), and \( l \) represent the electrical resistance, cross-sectional area, and length of the sample, respectively. At room temperature, the material shows a higher resistivity of 3.35 Ω m and a lower resistivity of 0.9 Ω m at 200 °C.

The Seebeck coefficient of the ST sample was measured from room temperature to 475 K and is shown in Figure 4. The “S” value of the ST increases as the temperature increases,

Figure 3. Electrical resistivity of the ST crystal.
indicating the semiconductor behavior. The ST sample exhibits a good Seebeck coefficient at a low temperature (313 K), i.e., 175 μV K⁻¹, and also at a higher temperature (450 K), the value increases dramatically to 210 μV K⁻¹. The obtained positive sign of the Seebeck coefficient of the ST confirms to be a p-type semiconductor and indicates that holes are the majority carriers. To be more precise, the Fermi level of the ST is present near the valence band. The measured Seebeck coefficient is slightly higher than those of nanomaterials reported by Goncalves et al. and Qin et al., with a higher charge carrier concentration than those of an ST thin film (∼191 μV K⁻¹) and nanomaterials (∼200 μV K⁻¹). At a measured range of temperatures, the slightly higher Seebeck coefficient of the ST material can be attributed to the higher crystalline nature of the samples as observed from high intensity diffraction peaks in the XRD patterns.

The electrical properties of the as-grown ST single crystal were determined using Hall measurement as shown in Figure 5. The Hall coefficient of the ST crystal exhibits a positive sign and further supports the results obtained from the Seebeck coefficient. The Hall carrier concentration of the ST crystal is 2 \times 10^{14} at room temperature; when increasing the temperature simultaneously, the carrier concentration also increases up to 9.8 \times 10^{14} at 350 K.

The thermal conductivity and diffusivity of the grown ST single crystal are shown in Figure 6. These measurements were done with the function of temperature ranging from room temperature to 300 °C by using a square-shaped crystal with a dimension of 8 mm × 8 mm. The thermal conductivity of the ST crystal gradually decreases with increasing temperature. As can be seen, the thermal conductivity of the ST crystal is low at a higher temperature due to the layered growth, which may have enhanced the phonon interaction. The ST crystal displays the total thermal conductivity of 1.8 W/m K at 308 K, and it decreases to 1.157 W/m K at 573 K. The thermal conductivity of the materials is based on effects of electron \( (K_e) \) and phonons \( (K_l) \). The electronic thermal conductivity of the materials is derived from the standard Wiedemann–Franz law \( (expression 2) \),

\[
k_e = L \sigma T
\]

where \( L \) is the Lorentz number, \( T \) is the absolute temperature, and \( \sigma \) is the electrical resistivity. The lattice thermal conductivity is extracted from the total thermal and calculated

![Figure 4. Seebeck coefficient of ST pellets.](image)

![Figure 5. Temperature-dependent carrier concentration and mobility.](image)

![Figure 6. Thermal conductivity and diffusivity of the ST crystal.](image)
thermal conductivity values. The total $K$ value decreases as a function of temperature because of the phonon–phonon scattering with structural defects in the crystal, which has contributed to a low thermal conductivity. Figure 7 depicts the $K_e$ and $K_l$ thermal conductivity of the grown ST crystal.

The power factor of the ST crystal was calculated using the values of Seebeck coefficient and electrical resistivity. Figure 8 shows the thermoelectric power factor of the ST single crystal as a function of temperature. The value of the power factor is 0.55 mW K$^{-2}$ m$^{-1}$ at room temperature. When the temperature increases, the power factor value is decreasing up to 390 K. Further, when the temperature increases up to 460 K, the power factor value is also relatively increasing and is found to be 0.7 mW K$^{-2}$ m$^{-1}$ at 460 K, which is relatively higher than lower temperature results.

The figure of merit (ZT) value was calculated using the above-measured properties like the Seebeck coefficient, electrical resistivity, and thermal conductivity of the grown ST single crystal. Figure 9 shows the ZT of the ST single crystal versus the function of temperature. The calculated dimensionless ZT value is small for the ST crystal, which is slightly increasing as a function of temperature. These kinds of low-ZT materials would be used for power generation applications. 

**CONCLUSIONS**

A single-phase ST material was successfully synthesized through the melting technique. The ST single crystal was successfully grown with an in-house-built Bridgman–Stockbarger system. The grown crystal crystallizes in a rhombohedral crystal system with the space group $R\bar{3}$m. The presence of elemental and oxidation states was confirmed. The grown ST crystal exhibits an electrical resistivity of 0.9 $\Omega$ m at 200 $^\circ$C, and the Seebeck coefficient value is found to be high at 200 $^\circ$C, that is, 210 $\mu$V K$^{-1}$. The obtained power factor value of the ST crystal is 0.7 mW K$^{-2}$ m$^{-1}$ at 460 K.

**EXPERIMENTAL PROCEDURE**

**Synthesis of Sb$_2$Te$_3$.** The Sb$_2$Te$_3$ (ST) single crystal was grown using a modified Bridgman–Stockbarger technique. Highly pure elements such as antimony (Sb; 99.9999%) and tellurium (Te; 99.9999%) were used without any further purification. Elements were weighted in a stoichiometric ratio of 2:3, and the materials were loaded into the quartz ampoule. The loaded ampoule was evacuated and sealed. The sealed ampoule was transferred to the vertical Bridgman–Stockbarger furnace. The furnace was heated up to the melting point of the ST material. The bulk growth of high-quality TE single crystals is a challenging task for crystal growers, because the solid–liquid interface and the optimization of temperature gradients are very difficult to control. In addition, the growth parameters such as growth rate and temperature gradient are optimized. The ampoule was rotated at a steady rate of 5 rpm and moved with a translation rate of 0.2 mm/h. The ST material was solidified, and the furnace was cooled to room temperature at the rate of 20 $^\circ$C/h. The as-grown and cut-polished single crystals are shown Figure 10a,b, respectively.

**Growth of the Single Crystal.** The synthesized ST materials were crushed into fine powder and loaded in the growth ampoule. The ampoule was sealed under vacuum. The sealed ampoule was transferred to the vertical Bridgman–Stockbarger furnace. The furnace was heated up to the melting point of the ST material. The bulk growth of high-quality TE single crystals is a challenging task for crystal growers, because the solid–liquid interface and the optimization of temperature gradients are very difficult to control. In addition, the growth parameters such as growth rate and temperature gradient are optimized. The ampoule was rotated at a steady rate of 5 rpm and moved with a translation rate of 0.2 mm/h. The ST material was solidified, and the furnace was cooled to room temperature at the rate of 20 $^\circ$C/h. The as-grown and cut-polished single crystals are shown Figure 10a,b, respectively.
Figure 10. (a) As-grown ST single crystal; (b) 8 mm × 8 mm sliced crystal (the figure is photographed by A.R.).

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**Notes**

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