Resonant Bonding, Multiband Thermoelectric Transport, and Native Defects in n-Type BaBiTe$_{3-x}$Se$_x$ ($x = 0$, 0.05, and 0.1)

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ABSTRACT: The unique crystal structure of BaBiTe$_3$ containing Te···Te resonant bonds and its narrow band gap motivated the systematic study of the thermoelectric transport properties of BaBiTe$_{3-x}$Se$_x$ ($x = 0$, 0.05, and 0.1) presented here. This study gives insight in the chemical bonding and thermoelectric transport properties of BaBiTe$_x$. The study shows that the presence of Te···Te resonant bonds in BaBiTe$_x$ is best described as a linear combination of interdigitating (Te$^{−1}$)$_2$ side groups and infinite Te$_n$ chains. Rietveld X-ray structure refinements and extrinsic defect calculations reveal that the substitution of Te by Se occurs preferentially on the Te4 and Te5 sites, which are not involved in Te···Te bonding. This work strongly suggests that both multiband effects and native defects play an important role in the transport properties of BaBiTe$_{3-x}$Se$_x$ ($x = 0$, 0.05, and 0.1). The carrier concentration of BaBiTe$_x$ can be tuned via Se substitution (BaBiTe$_{3-x}$Se$_x$ with $x = 0$, 0.05, and 0.1) to values near those needed to optimize the thermoelectric performance. The thermal conductivity of BaBiTe$_{3-x}$Se$_x$ ($x = 0$, 0.05, and 0.1) is found to be remarkably low (ca. 0.4 W m$^{-1}$K$^{-1}$ at 600 K), reaching values close to the glass limit of BaBiSe$_3$ (0.34 W m$^{-1}$K$^{-1}$) and BaBiTe$_3$ (0.28 W m$^{-1}$K$^{-1}$). Calculations of the defect formation energies in BaBiTe$_3$ suggest the presence of native Bi$_{Bi_{\text{ff}}}$ and Te$_{Bi_{\text{ff}}}$ antisite defects, which are low in energy and likely responsible for the native n-type conduction and the high carrier concentration (ca. 10$^{20}$ cm$^{-3}$) found for all samples. The analyses of the electronic structure of BaBiTe$_2$ and of the optical absorption spectra of BaBiTe$_{3-x}$Se$_x$ ($x = 0$, 0.05, 0.1, and 3) strongly suggest the presence of multiple electron pockets in the conduction band (CB) in all samples. These analyses also provide a possible explanation for the two optical transitions observed for BaBiTe$_3$. High-temperature optical absorption measurements and thermoelectric transport analyses indicate that bands higher in the conduction band converge with the conduction band minimum (CBM) with increasing temperature and contribute to the thermoelectric transport properties of BaBiTe$_x$. This multiband contribution can account for the absence of multiband effects in the thermoelectric transport properties of BaBiTe$_{3-x}$Se$_{0.1}$.

INTRODUCTION

Polychalcogenides exhibit a strikingly diverse crystal chemistry due to the formation of homonuclear and often resonant or hypervalent bonds between negatively charged chalcogen atoms (Q). This highly diverse anion chemistry led to the discovery of a vast number of new compounds with interesting physical properties over the past decades. Within the family of polychalcogenides there are several examples with promising thermoelectric properties such as HfTe$_6$, Ba$_3$Cu$_{14}$S$_{12}$Te$_{12}$, BaCu$_2$Se$_4$Te$_{12}$, and A$_2$BaCu$_2$Te$_{14}$ (A = K, Rb, Cs). Many of them possess low thermal conductivities, which can be well explained by their complex crystal structures, while their overall electronic transport properties are often poorly understood. Since it was realized that multivalley bands and band convergence of multiple valence or conduction bands can result in high thermoelectric efficiencies, it is of interest to look deeper into the thermoelectric transport properties of polychalcogenides with complex crystal structures since many of them possess complex electronic structures and inherently low thermal conductivities.

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The polytetrafluoroethylene compound BaBiTe$_3$ isostructural to BaBiSe$_3$ and BaSbTe$_3$ was first discovered by Chung et al. and its thermoelectric transport properties were measured on single crystals. The unique part of the crystal structure of BaBiTe$_3$ is the parallel stripes of weak Te···Te bonding, the nature of which is still not entirely understood. BaBiTe$_3$ is an ideal candidate for fulfilling the requirements of a phonon glass and an electron crystal, which according to Slack results in both a low thermal and a high electrical conductivity needed for thermoelectricity.

Low-temperature thermoelectric measurements of both p- and n-type single crystalline BaBiTe$_3$ and electronic band structure calculations gave a minimum thermal conductivity, and optimize its carrier containing Ba or Tl.18 thermal conductivity similar to previously studied compounds heavy Ba atoms and weak Te···Te bonding result in a low thermal conductivity similar to previously studied compounds heavy Ba atoms and weak Te···Te bonding.

Understanding the chemical bonding is crucial since the type of bonding (metallic, covalent, ionic) can significantly affect the physical properties by controlling the degree of electron delocalization. The main objectives for alloying BaBiTe$_3$ with Se were to reduce its thermal conductivity, determine the minimum thermal conductivity, and optimize its carrier concentration.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Synthesis. An amount of 10 g of fine polycrystalline powders of BaBiTe$_3$, Se$_x$ (x = 0, 0.05, 0.1, and 3) was obtained by ball milling (700 rpm, 15 milling cycles with a milling time of 2 min per cycle) starting from stoichiometric mixture of Ba pieces (Alfa Aesar, 99+%), Bi powder (Alfa Aesar, 99.99%), Se powder (Alfa Aesar, 99.99%) and Te powder (Alfa Aesar, 99.999% + 6%). All elements were stored under inert atmosphere, and Se shots and Te lumps were freshly powdered before having measured the thermoelectric properties.

Electrical resistivity ($\rho$), hall carrier concentration ($n$), and mobility ($\mu$) were measured on an in-house built measurement system using the van der Pauw method and pressure-assisted Mo contacts. A magnetic field of 2T was applied during the hall measurements. The Seebeck coefficient was measured using a home-built measurement system and Chromel-Nb thermocouples.

Optical Absorption Measurements. Mid-Infrared (~0.08–0.7 eV) diffuse reflectance (R) spectra of BaBiTe$_3$, Se$_x$ (x = 0, 0.05, and 0.1) were collected under argon atmosphere in the temperature range 300–500 K with a Nicolet 6700 FTIR Spectrometer equipped with a Praying Mantis attachment and a high-temperature stage from Harrick Scientific Instruments. A KBr standard was used as reference. The room temperature diffuse reflectance of BaBiSe$_3$ was recorded with a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer operating from 200 to 2500 nm using BaSO$_4$ as a nonabsorbing reference sample. The absorption spectra ($\alpha$/s) were obtained using the Kubelka–Munk function, which gives a relationship between R and the absorption coefficient ($\alpha$) and scattering coefficient (s) through

$$\frac{\alpha}{s} = \frac{(1 - R)^2}{2R}$$

Speed of Sound Measurements and Evaluation of Cahill’s Glass Limit of the Thermal Conductivity ($k_{glass}$) and the Debye Temperature ($\theta_D$) of BaBiTe$_3$ and BaBiSe$_3$. The longitudinal and transversal components of the speed of sound ($v_l$ and $v_t$) were measured applying the pulse–echo method. A piezoelectric transducer coupled to the sample first sends the initial pulse and then acts as a receiver measuring the echoed reflections (for details see Supporting Information). The speed of sound ($v_s$) was calculated from the longitudinal and transversal components $v_l$ and $v_t$ as follows:

$$v_s = \left[\frac{1}{3}(\frac{2}{v_l^3} + \frac{1}{v_t^3})\right]^{-1/3}$$

From the speed of sound the Debye temperature ($\theta_D$) and Cahill’s glass limit of the thermal conductivity ($k_{glass}$) were calculated as follows:

$$k_{glass} = \frac{1}{2} \left[\frac{\omega_L}{k_B}\right]^{1/3}$$

where $\omega_L$ is the Debye frequency.
\[ \omega_{n, \beta} = \psi \left( \frac{6\pi^2 \xi^3}{V} \right) \]

and where \( V \) corresponds to the unit cell volume per atom. The corresponding values of \( v_\sigma \), \( v_\pi \), \( \theta_{\sigma\pi} \), and \( \omega_{n, \beta} \) can be found in the Supporting Information.

**Electronic Structure, Defect, and COHP Calculations.** All density functional theory computations were performed using the Vienna ab initio software package (VASP), \(^{36,39}\) generalized gradient approximation as implemented by Perdew, Burke, and Ernzerhof (PBE), \(^{13}\) and a kinetic energy cutoff of 520 eV. A scissor (operator) shift was applied to the DFT band structure to correct the band gap and facilitate the comparison with experimental results. This correction is based on the empirical band gap obtained from optical absorption measurements (0.26 eV) and is consistent with the Goldsmid–Sharp band gap \( (E_g = 2eS_{\text{max}}T_{\text{max}}) \) of ca. 0.23 eV. For bulk calculations, the Brillouin zone was sampled by a \( 6 \times 2 \times 2 \) k-point mesh, while for the defect calculations a k-point mesh of \( 2 \times 2 \times 2 \) and a \( 3 \times 1 \times 1 \) supercell were used. A force convergence criterion of 0.005 eV/Å was adopted for all structural relaxations. The Crystal Orbital Hamilton population (COHP) curves were calculated using the LOBSTER \(^{42}\) software. The defect formation energy \( D \) in a charge state \( q \) was calculated according to

\[ E_q[\text{D}^+] = E[\text{D}^+] + E_{\text{corr}}[\text{D}^+] - E[\text{bulk}] - \sum_i n_i \mu_i \]

\[ + q \left( \epsilon_{\text{VBM}} + \Delta \epsilon \right) + \Delta \epsilon_{\text{F}} \]

where \( E[\text{D}^+] \) and \( E[\text{bulk}] \) represent the total energy of the supercell with defects \( D \) in the charge state \( q \) and without any defects, respectively, \( n_i \) is the number of removed \( (n_i < 0) \) or added \( (n_i > 0) \) \( \delta \)-type atoms, and \( \mu_i \) is the chemical potential. \( \epsilon_{\text{VBM}} \) is the energy of the valence band maximum (VBM), and \( \Delta \epsilon_{\text{F}} \) is the Fermi energy (chemical potential) of the electrons relative to \( \epsilon_{\text{VBM}} \). \( E_{\text{corr}}[\text{D}^+] \) and \( \Delta \epsilon \) are correction terms for the spurious image–image interaction and potential alignment. \(^{44}\)

The chemical potential of the elements was obtained from a stable stoichiometry, while for delocalized defects, only a potential alignment between the bulk and the neutral state was included. No band gap corrections have been applied on the defect computations.

**Calculations of the Optical Absorption Coefficient.** The optical absorption coefficient (\( \alpha \)) of BaBiTe\(_3\) was calculated as a function of energy using the DFT (PBE) method and the random phase approximation approach (RPA). We neglect excitonic effects which we expect to be small in this material. A scissor (operator) shift was applied to the DFT band structure to correct the band gap and set it consistently to the experimental value. A very dense k-point mesh of \( 34 \times 9 \times 9 \) corresponding to 450 k-points in the irreducible Brillouin zone is utilized to compute \( \alpha \). It is worth noting that only direct (i.e., no change in \( k \)-space) transitions are considered. Details concerning this type of calculation can be found in the Supporting Information of ref. 49.

**RESULTS AND DISCUSSION**

**BaBiTe\(_3\): Crystal Structure and Te···Te Bonding.** The crystal structure of BaBiTe\(_3\) (cf. Figure 1) was first determined by Chung et al. \(^{16}\) and the authors discussed two alternative Te···Te bonding situations, which can both describe the chemical bonding in the crystal structure.

Their discussion is based on the Te···Te contacts (Te\(_2\)···Te\(_6\): 3.098 (2) Å and Te\(_2\)···Te\(_2\): 3.170 (2) Å) \(^{51}\) found between the rod-shaped columns \([\text{Bi}_4\text{Te}_{10}\text{]}_{\infty}\) segments, which are built up by edge-sharing Bi\(_6\) octahedra. These Te···Te distances are larger compared to those found for normal covalent Te···Te single bonds (2.69–2.80 Å) \(^{50}\) but well below typical van der

![Figure 1. Crystal structure of BaBiTe\(_3\) (black, Ba; light gray, Bi; dark gray, Te).](image-url)

![Figure 2. Previously described Te···Te bonding situations: (a) Te\(_n\) chains and (b) interdigitating (Te\(_{3}^{-}\))\(_2\) side groups and (c) electron localization function of Te\(_2\) and Te\(_6\) (left) and \(-p\)COHP curves of the Te\(_2\)···Te\(_2\) and Te\(_2\)···Te\(_6\) pairs (right) showing bonding interactions between Te\(_2\)···Te\(_2\) and Te\(_2\)···Te\(_6\). (d) Te···Te resonant bonding, which can be understood as a linear combination between (a) and (b) and which involves three-center–four-electron (3c–4e) bonds. The bonding situation in (d) is based on results from \(-p\)COHP and ELF calculations shown in (c). This new Te···Te bonding situation represents an electron delocalization over the Te\(_2\) and Te\(_6\) atoms, which reduces electrostatic repulsion between the Te\(_2\) and the Te\(_6\) atoms by minimizing their negative charge.](image-url)
calculated and concluded, based on these findings, that the crystal structure is better described as \([\text{Bi}_4\text{Te}_{10}(\text{Te}_2)_{3x}]\) rods with \((\text{Te}^{3+})\), side groups and that there are no Te\(_6\) chains in the BaBiTe\(_3\) crystal structure.

Our bonding analysis (cf. Figure 2c) focuses on the bonding between Te\(_2\) and Te\(_6\). It is based on the evaluation of the electron localization function (ELF) and the crystal orbital Hamilton population (COHP) from density functional theory (DFT) in the generalized gradient approximation (GGA) computations. It unambiguously shows Te\(_2\)–Te\(_2\) and Te\(_2\)–Te\(_6\) bonding interactions consistent with the similar interatomic Te\(_2\)–Te\(_2\) and Te\(_2\)–Te\(_6\) distances. This new bonding situation is shown in Figure 2d and can be rationalized as a linear combination of the two previous descriptions of the bonding situation is shown in Figure 2d and can be rationalized as a linear combination of the two previous descriptions of the bonding situation.

Hence, the former are slightly weaker, and the part of the BaBiTe\(_3\) crystal structure that is dominated by Te\(_2\)–Te\(_2\) interactions compared to those between the Te\(_2\) atoms.

Preferential Site Substitution of Se on the Te\(_4\) and Te\(_5\) Sites. The crystal structure of BaBiTe\(_3\) was confirmed by PXRD and subsequent Rietveld refinements (cf. Figure 3) based on the structural model obtained from a previous single crystal structure analysis of BaBiTe\(_3\).

The site occupancy factors (s.o.f.) were refined for the Se substituted variants and we find that for x = 0.05 Se substitutes Te on the Te\(_5\) site (s.o.f. on Te\(_5\):0.96/0.04 Te/Se), while Se substitutes Te on the Te\(_4\) and Te\(_5\) sites for x = 0.1 with a slight preference toward Te\(_5\) (s.o.f. on Te\(_4\):0.9/0.1 Te/Se and s.o.f. on Te\(_5\):0.78/0.22 Te/Se), and all other sites are fully occupied by Te. The corresponding results of the refinements are summarized in Table 1, and the refined site occupancy factors are visualized exemplarily for x = 0.1 in Figure 4.

### Table 1. Rietveld X-ray Refinement Results for BaBiTe\(_3\), BaBiTe\(_3\), and BaBiTe\(_3\), Se\(_{0.1}\) (x = 0, 0.05, 0.1)

<table>
<thead>
<tr>
<th>nominal composition</th>
<th>BaBiTe(_3)</th>
<th>BaBiTe(<em>3), Se(</em>{0.05})</th>
<th>BaBiTe(<em>3), Se(</em>{0.1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>space group</td>
<td>P2(_1), P2(_1), P2(_1)</td>
<td>P2(_1), P2(_1), P2(_1), (No. 19)</td>
<td>P2(_1), P2(_1), P2(_1), (No. 19)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>4.6147(1)</td>
<td>4.6103(1)</td>
<td>4.6105(1)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>17.0365(4)</td>
<td>17.0287(4)</td>
<td>17.0171(5)</td>
</tr>
<tr>
<td>a (Å)</td>
<td>5.1934(1)</td>
<td>5.1927(1)</td>
<td>5.1923(1)</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>1439</td>
<td>1435</td>
<td>1430</td>
</tr>
<tr>
<td>(\rho_{calc}) (g cm(^{-3}))</td>
<td>6.733</td>
<td>6.746</td>
<td>6.702</td>
</tr>
<tr>
<td>radiation CuK(<em>\alpha), (\lambda</em>{1/2})</td>
<td>1.54060/1.54439 Å</td>
<td>1.54060/1.54439 Å</td>
<td>1.54060/1.54439 Å</td>
</tr>
<tr>
<td>2&amp; limits (deg)</td>
<td>5.01–119.99</td>
<td>5.01–119.99</td>
<td>5.01–119.99</td>
</tr>
<tr>
<td>(R_b)</td>
<td>0.041</td>
<td>0.030</td>
<td>0.0401</td>
</tr>
<tr>
<td>(R_{noBS})</td>
<td>0.048</td>
<td>0.036</td>
<td>0.0464</td>
</tr>
<tr>
<td>(\chi^2)</td>
<td>1.48</td>
<td>1.62</td>
<td>1.64</td>
</tr>
</tbody>
</table>

The clear changes in the lattice parameters (cf. Table 1) provide proof for a successful substitution of Te by Se, which can be confirmed by complementary EDS analyses. The elemental compositions extracted from EDS analyses are provided in Table 2, and the corresponding EDS spectra can be found in the Supporting Information.

Since there is a preferential site substitution on the Te sites that is not involved in Te\(_2\)–Te\(_2\) bonding, it can be concluded that a Se substitution of Te\(_2\) and/or Te\(_6\) atoms would destabilize the crystal structure and is therefore energetically not favorable. This is in good agreement with the extrinsic defect calculations (cf. Supporting Information), which are further discussed in the section Defect Chemistry of BaBiTe\(_3\) and its Se Substituted Variants.

Multiple Electron Pockets in the Conduction Band of BaBiTe\(_3\) and Orbital Character of the Conduction and Valence Band Edges. The electronic structure of BaBiTe\(_3\) was calculated and described previously.\(^{16,28}\) Both studies could not entirely clarify the nature of the two transitions at \(\sim 0.28\) eV (transition 1) and \(\sim 0.42\) eV (transition 2) observed by diffuse reflectance (DR) measurements. This inspired us to recalculate the electronic structure in order to better understand the thermolectric transport properties of BaBiTe\(_3\) and the unusual shape of its experimental optical absorption spectrum, which is discussed in the section Band Convergence and an Explanation for the Two Optical Transitions. It is important to note that spin–orbit coupling (SOC) does not significantly affect the
Table 2. Experimental Compositions Obtained from EDS Analyses after Thermoelectric Characterization

<table>
<thead>
<tr>
<th>nominal composition</th>
<th>Ba (atom %)</th>
<th>Bi (atom %)</th>
<th>Te (atom %)</th>
<th>Se (atom %)</th>
<th>exp. composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaBiTe$_3$</td>
<td>20.18</td>
<td>20.86</td>
<td>58.96</td>
<td>-</td>
<td>Ba$<em>{1.03}$Bi$</em>{1.06}$Te$_3$</td>
</tr>
<tr>
<td>BaBiTe$<em>{2.90}$Se$</em>{0.10}$</td>
<td>19.99</td>
<td>21.03</td>
<td>58.12</td>
<td>0.86</td>
<td>Ba$<em>{1.01}$Bi$</em>{1.07}$Te$<em>{2.90}$Se$</em>{0.09}$</td>
</tr>
<tr>
<td>BaBiTe$<em>{2.95}$Se$</em>{0.05}$</td>
<td>19.86</td>
<td>21.11</td>
<td>57.16</td>
<td>1.87</td>
<td>Ba$<em>{1.01}$Bi$</em>{1.06}$Te$<em>{2.95}$Se$</em>{0.04}$</td>
</tr>
</tbody>
</table>

overall band structure of BaBiTe$_3$ (cf. Figure S3 in the Supporting Information).28

It does, however, significantly decrease the band gap. For narrow band gap materials it is difficult to obtain accurate band gaps from DFT-PBE calculations, which is why a scissor (operator) shift was applied to correct the band gap to the empirical value of 0.26 eV based on the optical band gap (experimental). This value is also consistent with calculations including SOC (cf. Figure S3 in the Supporting Information) and the Goldsmid—Sharp band gap (ca. 0.23 eV), which is discussed in the section Thermoelectric Transport Properties of BaBiTe$_{3−x}$Se$_x$ ($x = 0, 0.05, 0.1$).

Our results (cf. Figure 5a) show three electron pockets (CB$_1$, CB$_2$, and CB$_3$) that lie close in energy in a range of only 100 meV and which are also present in Se substituted variants of BaBiTe$_3$ (cf. Supporting Information). CB$_1$ and CB$_2$ are located along the IZ and IX directions, allowing nearly direct transitions from the VBM, while CB$_3$ is located along the SY direction allowing indirect transitions from the VBM.

The three electron pockets signify a material system with multiple valleys, which is an important feature since complex band structures with multivalley bands (i.e., a large valley degeneracy $N_v$) and contributions of multiple conduction and/or valence bands can lead to high-efficiency thermoelectric materials as it was demonstrated for SnSe$_x$$_{52}$ CoSb$_{3x}$$_{53}$ and PbTe$_{1−x}$Se$_x$$_{15}$

Knowing the atomic and orbital contributions to the band edges is important in order to understand which part of the crystal structure governs the electronic transport. This is especially true in compounds where ionic and covalent bonding coexists and where it is often assumed that the covalent part of the structure dominates the electronic transport. The band edges in BaBiTe$_3$ are dominated by Bi and Te states (cf. Figure 5a). The strongest contribution to the valence band edge comes from the Bi$6p$–Te$5p$ and Te$5p$–Te$5p$ bonding states, while their corresponding antibonding states are the main contributors to the conduction band edge (cf. Figure 6). These

![Figure 6. COHP curves of BaBiTe$_3$ containing (a) Bi–Te interactions and (b) Te–Te interactions. (c) shows an MO diagram reflecting the COHP analysis.](Image)

Bi$6p$–Te$5p$ and Te$5p$–Te$5p$ contributions are also visualized in Figure 5 (other contributions are not shown for clarity reasons). Figure 5b,c shows the charge density distribution of the CBM and the VBM containing only the Bi$6p$–Te$5p$ and Te$5p$–Te$5p$ contributions. This representation allows visualizing the orbital contributions of each atom to the CBM and VBM and hence provides a more detailed description of the band edges.

The main Bi$6p$ and Te$5p$ contributions to the CBM come from the Te2 and Bi2 atoms, and those contributing to the VBM come from the Te3, Te4, and Te5 atoms. The Bi6s and Te5s states (cf. Figure 6) are also important to obtain a more complete picture.

These mix with the Te5p states, leading to significant contributions of Bi6s–Te5p antibonding states to the valence band edge. The conduction band edge also shows significant contributions of antibonding Bi6p–Te5s states. Our COHP analysis and the MO diagram (cf. Figure 6) provide a comprehensive picture of all covalent bonding interactions in BaBiTe$_3$ and they show to which extent the different orbitals contribute to the electronic transport. However, Figure 6 entirely neglects the ionic part of the crystal structure, which is not shown for clarity reasons. A detailed COHP analysis of the ionic part of the crystal structure can be found in the Supporting Information, and it shows significant contributions...
of the Ba6s–Te6p bonding states and Ba6p–Te6p antibonding states to the valence band edge.

Hence, a complete COHP analysis reveals that both the covalently and the ionically bonded parts as well as the Bi lone pairs of the crystal structure are expected to play a role in the electronic transport of BaBiTe3.

Multiple Electron Pockets in the Conduction Band of Se Substituted Variants of BaBiTe3. Optical absorption measurements of polycrystalline BaBiTe3 (cf. Figure 7a)

![Figure 7](image)

confirm the results obtained for single crystalline BaBiTe3 in 1997, which made it possible to use this compound as a standard for further optical absorption measurements of BaBiTe2.95Te0.05, BaBiTe2.9Se0.1, and BaBiSe3 (cf. Figure 7a).

These show that the optical band gap does not change significantly for compositions up to x = 0.1, while BaBiSe3 has only one transition at ~0.90 eV (cf. Figure 7a), which corresponds to an optical band gap significantly larger compared to those of BaBiTe2.95–xSe0.05 (x = 0, 0.05, and 0.1). The two optical transitions observed for BaBiTe3 are also found for the Se substituted variants with x = 0.05 and 0.1 as it is illustrated in Figure 7b for x = 0.05, and the energies of the two transitions are shown as a function of Se content in Figure 7c.

Band Convergence and an Explanation for the Two Optical Transitions. Up to now we provided a comprehensive picture of the bonding interactions in BaBiTe3 and its electronic structure including orbital contributions and we showed that BaBiTe3–xSe0.05 (x = 0, 0.05, and 0.1) are multiband systems. Now, we will relate the experimentally observed optical transitions to the electronic structure in order to explain the two optical transitions observed experimentally. These results are then used to demonstrate that band convergence occurs in BaBiTe2.95Se0.05.

Analyzing transition 2 of BaBiTe2.95Se0.05 by the Tauc method (cf. Figure 7d) revealed that this transition is direct, which excludes the possibility of indirect VBM-CB2 and VBM-CB3 transitions being associated with transition 2. Figure 8a shows the electronic structure and density of states (DOS) of BaBiTe3, including two transitions, which can qualitatively explain the shape of the experimental absorption spectra shown in Figure 7ab.

This is also quantitatively validated in Figure 8bc presenting the calculated joint density of states and optical absorption spectrum of BaBiTe3, respectively. These calculations were performed assuming that BaBiTe3 is undoped (or has a very low carrier concentration). From these calculations we can conclude that transition 1 and 2 correspond to transitions from the VBM to CB1 and to bands higher in the conduction band next to CB2. These bands are located along the ΓY direction between CB1 and CB2 (cf. Figure 8a).

Transition 2 is direct, which is consistent with the Tauc analysis shown in Figure 7d. This transition is significantly stronger than transition 1 in terms of intensity. This can be explained by the lower dispersion of the bands higher in the conduction band compared to those at CB1. A lower dispersion (i.e., when the bands are more flat) results in a larger density of states (cf. Figure 8a). This is why the number of optical transitions at 0.26 eV (transition 1) is smaller than at 0.5 eV (transition 2). This is reflected in the joint density of states (cf. Figure 8c), which is a measure for the amount of states in the valence and conduction band available for a photon of a given energy hν to interact with. The larger the available states, the higher the transition rate and the larger the intensity of the transition. Transition 2 is more intense than transition 1 since more states are available in the conduction band compared to transition 1.

High-temperature optical absorption measurements of BaBiTe2.95Se0.05 (cf. Figure 9a) show that transition 2 moves to lower energies with respect to temperature, while the energy of transition 1 stays constant (cf. Figure 9b).

Hence, the bands higher in the conduction band move toward lower energies. At ca. 830 K these bands can be considered as being fully converged with CB1. Figure 9c shows that the band offset between CB1 and the bands higher in the conduction band (located along the ΓY direction between CB1 and CB2) slightly increases with the Se content. The band offset was extracted from the optical absorption measurements (cf. Figure 7c).
Thermoelectric Transport Properties of BaBiTe$_{2.95}$Se$_{0.05}$ ($x = 0, 0.05, 0.1$). The efficiency of a thermoelectric material is defined by the thermoelectric figure of merit ($zT$).

\[ zT = \frac{S^2}{\rho \kappa} T \]  

(7)

The thermal conductivity ($\kappa$) contains the phononic ($\kappa_{ph}$), electronic ($\kappa_{e}$), and bipolar ($\kappa_{bip}$) contribution. Seebeck coefficient ($S$), electrical resistivity ($\rho$), and the electronic and bipolar contribution of $\kappa$ are interdependent, while $\kappa_{ph}$ is mostly independent of the other quantities. The thermoelectric properties of polycrystalline BaBiTe$_{2.95}$Se$_{0.05}$ and that the band offset increases with the Se content.

Seebeck coefficient and thermal conductivity were measured out of plane, while the electrical resistivity was measured in plane. The Seebeck coefficient (cf. Figure 10a) of all compounds increases up to ca. 550 K and shows a “roll-over” between 550 and 600 K due to the activation of minority charge carriers. The maximum of the Seebeck coefficient ($S_{\text{max}}$) at the temperature $T_{\text{max}}$ is almost independent of the Se content, which is consistent with the optical absorption spectra showing no significant changes in the optical band gap up to $x = 0.1$.

The Goldsmid–Sharp band gap ($E_g = 2eS_{\text{max}}T_{\text{max}}$) of all compounds measures ca. 0.23−0.25 eV, which agrees well with the optical band gap (0.26 eV).

Increasing the Se content leads to higher Seebeck coefficients, which is consistent with the increase in resistivity (cf. Figure 10b). BaBiTe$_x$, BaBiTe$_{2.95}$Se$_{0.05}$, and BaBiTe$_{2.9}$Se$_{0.1}$ show a small reduction in thermal conductivity (cf. Figure 10c) with an increasing Se content as expected from point defect scattering. This effect could also be due to the slightly different densities of the samples. However, because of the complex low symmetry structure (few acoustic phonons) and large anharmonicity the lattice thermal conductivity is already low (0.41(2) W m$^{-1}$ K$^{-1}$ at 600 K). The thermal conductivity (not the diffusivity) of pristine BaBiTe$_x$ was previously measured on single crystals using a modified pulse technique originally developed by Maldonado. The values we obtain for BaBiTe$_x$ using the Dulong Petit approximation compare well for temperatures below ca. 150 K, where radiation effects due to insufficient heat dissipation can be neglected. It is therefore justifiable to use the Dulong–Petit approximation. All the title compounds possess remarkably low thermal conductivities close to the glass limit (cf. Figure 10c) of BaBiSe$_x$ (0.34 W m$^{-1}$ K$^{-1}$) and BaBiTe$_x$ (0.28 W m$^{-1}$ K$^{-1}$). The glass limit is slightly higher for BaBiSe$_x$ since both the longitudinal and transversal components of the speed of sound are larger for BaBiSe$_x$ ($v_L = 1535$ m/s, $v_T = 2863$ m/s) compared to BaBiTe$_x$ ($v_L = 1462$ m/s, $v_T = 2536$ m/s), which can be attributed to the lower mass density of Se compared to Te and to softer bonds in BaBiSe$_x$. Hence, BaBiSe$_x$ can be expected to be more anharmonic compared to BaBiTe$_x$. Figure 11 shows the measured Hall mobility ($\mu$) and charge carrier concentration ($n$) of BaBiTe$_{2.95}$Se$_{0.05}$ ($x = 0, 0.05$, and 0.1). The electron mobility (ranging from 2 to 5 cm$^2$ V$^{-1}$ s$^{-1}$) generally decreases with temperature as expected from phonon scattering but may show grain boundary scattering at low temperature.

The carrier concentration of BaBiTe$_x$ is almost constant with temperature up to ca. 370 K and increases significantly between 370 and 600 K like one might see from the formation of charged defects. A similar trend can be observed for BaBiTe$_{2.95}$Se$_{0.05}$. The increase in carrier concentration, however, is less pronounced and is only significant for temperatures above ca. 500 K.

Increasing the Se content further results in an almost temperature independent carrier concentration for BaBiTe$_x$. The substitution of Te by Se does not affect the electron mobility in a systematic or significant way but results in a clear reduction in charge carrier concentration. This decrease in carrier concentration with Se content explains the increase in resistivity. The possible origin for such high carrier concentrations will be discussed in the section Defect Chemistry of BaBiTe$_x$ and Its Se Substituted Variants. The overall thermoelectric properties of BaBiTe$_x$ and BaBi-
multiband calculations of the electronic structure and optical absorption

Figure 11. (a) Hall mobility and (b) hall charge carrier concentration of BaBiTe3,Se0.1 (x = 0, 0.05, 0.1) as a function of temperature; (c) calculated zT as a function of hall carrier concentration: lines and symbols correspond to effective band models and experimental data points, respectively; (d) “Seebeck effective mass” (m*) as a function of temperature (line and symbols represent calculated m* obtained from interpolated and experimental Seebeck data, respectively). (b)–(d) show the contribution of CB2 for BaBiTe3,Se0.1 (x = 0, 0.05) in the form of an increase in carrier concentration and m* with temperature.

Table 2.56. Values for the three regions BaTe–Bi–Te phase diagram: (a) region 1: BaTe–Bi2Te3–BaBiTe3, (b) region 2: BaTe–Bi–Te–BaBiTe3, (c) region 3: Bi2Te3–Te–Bi2Te3–BaBiTe3.

Defect Chemistry of BaBiTe3 and Its Se Substituted Variants. The main reason for studying the defect chemistry of BaBiTe3,Se0.1 is the large charge carrier concentration observed, which points toward unintentional doping through native defects. The closely related Bi2Te3, Bi2Se3 and its solid solutions also have native defects that play an important role in their thermoelectric transport properties.56 Insights in the defect chemistry can help to explain why BaBiTe3 and its Se substituted variants are all n-type semiconductors and possibly predict whether intrinsic p-type samples can be obtained. We calculated the formation energies (E[D]) of intrinsic defects in BaBiTe3 in three different regions of the Ba–Bi–Te phase diagram (cf. Figure 12).

The values of allowed chemical potential are determined by the three regions BaTe–Bi–Te–BaBiTe3, BaTe–Te–BaBiTe3, and (c) region 3: Bi2Te3–Te–Bi2Te3–BaBiTe3.
and Bi₂Te₃⁻Te-BaBiTeₓ, which will be referred to as regions (a), (b), and (c). These different regions correspond to different thermodynamic conditions in which BaBiTeₓ is stable and are related to different synthesis conditions. Figure 12 plots the defect formation energy depending on the Fermi level for a series of intrinsic defects in different regions of chemical potentials. In all conditions, there are Bi₆⁺ and Te₆⁻ defects with negative formation energies close to the valence band maximum. These defects are electron donors compensating any attempt to dope the material p-type in equilibrium conditions. On the other hand, no negative formation energy defects are present close to the conduction band minimum indicating that the material has no electron killers. We conclude that BaBiTeₓ is thermodynamically favoring n-type conductivity and that any attempt to dope this p-type material will be challenging. This is in agreement with the n-type nature of the experimentally realized materials. Moreover, our work identifies the potential majority defects, Bi₆⁺, which are the lowest energy electron donors in all regions, probably leading to the observed n-type conduction.

In BaBiTeₓ, a second cation (Ba²⁺) is present, which is lacking in Bi₂Te₃ and which fundamentally changes the defect chemistry since antisite defects form more easily between two cations than between a cation and an anion. This is evident from the low formation energy of the Bi₆⁺ antisite defects in BaBiTeₓ. In n-type Bi₂Te₃ and Bi₂Se₃, TeBa⁺ and SeBi⁺ defects (under Se-rich conditions) have low formation energies and are possibly responsible for the observed n-type conduction in these compounds. The vacancies of Te and Se are also low in energy in Bi₂Te₉, while being much higher in energy than Bi₆⁺ in BaBiTeₓ. Interestingly, Bi₂Te₃ can easily be doped p- and n-type, while p-type doping of BaBiTeₓ is challenging due to the low formation energies of the Bi₆⁺ antisite defects.

Our defect calculations show that the defect chemistry of BaBiTeₓ differs significantly from the one in Bi₂Te₃ and the reason for the difference is the presence of Ba²⁺ as a second cation. The preferential site substitution of Se on the Te₄ and Te₅ sites presented above (cf. section Preferential Site Substitution of Se on the Te₄ and Te₅ Sites) motivated us to study the defect chemistry of Se substituted variants of BaBiTeₓ in order to explain this preference from an energetic point of view. Results of our extrinsic defect calculations can be found in the Supporting Information, and they revealed equally low formation energies close to zero for SeBiTe₄ and SeBiTe₅ defects, which explain the preferential site substitution on the Te₄ and Te₅ sites.

### CONCLUSION

The presence of Te···Te resonant bonds in BaBiTeₓ is best described as a linear combination of interdigitating (Te³⁻), side groups and infinite Teₙ chains. Complementary Rietveld refinements and extrinsic defect calculations show that the Se substitution preferentially occurs on the Te₄ and Te₅ sites, which are not involved in Te···Te bonding. Ab initio calculations of the electronic structure, optical absorption measurements, and an effective band model analysis of the thermoelectric transport properties of BaBiTeₓ⁻ₓSeₓ (x = 0, 0.05, 0.1) strongly suggest the presence of multiple conduction bands. These analyses also provide an explanation for the two optical transitions observed experimentally. Bands higher in the conduction band converge with the conduction band minimum with increasing temperature and contribute to the thermoelectric transport properties of BaBiTeₓ and BaBiTeₓ⁻ₓSeₓ. This multiband contribution can be considered as the reason for the ~50% higher zT at 617 K compared to BaBiTeₓ⁻ₓSe₀.₁ for which no such contribution was found. The increase in the band offset between the CBM and the bands higher in the conduction band with respect to the selenium content is one possible explanation for the absence of multiband effects in the thermoelectric transport properties of BaBiTeₓ⁻ₓSe₀.₁.

A detailed analysis of the defect chemistry of BaBiTeₓ suggests the presence of native Bi₆⁺ and Te₆⁻ defects at 0 K, and these are probably responsible for the observed n-type conduction. BaBiTeₓ is the first example of a mixed-valent chalcogenide with Te···Te resonant bonds, where its thermoelectric properties benefit from the contribution of multiple conduction bands. Hence, chalcogenides with resonant bonds are promising for continued investigations as new thermoelectric materials.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b04123.

Details on speed of sound measurements and evaluation of ωₓ, ωᵧ, and θₒ EDS spectra of all title compounds, results of extrinsic defect calculations, electronic structure calculations, COHP curves containing all Ba–Te interactions, and thermal diffusivities of BaBiTeₓ⁻ₓSeₓ (x = 0, 0.05, and 0.1) (PDF)

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Notes

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■ REFERENCES


