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Multiple Roles of Unconventional Heteroatom Dopants in Chalcogenide Thermoelectrics: The Influence of Nb on Transport and Defects in Bi$_2$Te$_3$

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ABSTRACT: Improvements in the thermoelectric performance of n-type Bi$_2$Te$_3$ materials to more closely match their p-type counterparts are critical to promote the continued development of bismuth telluride thermoelectric devices. Here the unconventional heteroatom dopant, niobium, has been employed as a donor in Bi$_2$Te$_3$. Nb substitutes for Bi in the rhombohedral Bi$_2$Te$_3$ structure, and exhibits multiple roles in its modulation of electrical transport and defect-induced phonon
scattering. The carrier concentration is significantly increased as electrons are afforded by
collovalent doping and formation of vacancies on the Te sites. Further, incorporation of Nb in the
pseudo-ternary Bi$_{2-x}$Nb$_x$Te$_3$ system increases the effective mass, $m^*$, which is consistent with
cases of “conventional” elemental doping in Bi$_2$Te$_3$. Lastly, inclusion of Nb induces both point and
extended defects (tellurium vacancies and dislocations, respectively), enhancing phonon scattering
and reducing the thermal conductivity. As a result, an optimum $zT$ of 0.94 was achieved in n-type
Bi$_{0.92}$Nb$_{0.08}$Te$_3$ at 505 K, which is dramatically higher than an equivalent undoped Bi$_2$Te$_3$ sample.
This study suggests that not only is Nb an exciting and novel electron dopant for the Bi$_2$Te$_3$ system,
but also that unconventional dopants might be utilized with similar effects in other chalcogenide
thermoelectrics.

1. INTRODUCTION

Energy conversion and storage are critical for the successful exploitation of renewable resources.
Thermoelectric materials have attracted extensive attention in the context of the direct
interconversion of heat and electricity.$^{1,2}$ The thermoelectric performance of a material can be
evaluated by the dimensionless figure of merit, $zT = S^2\sigma T / \kappa$, where $S$, $\sigma$, $\kappa$, and $T$ are the
Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature,
respectively.$^{3-6}$ Excellent electrical transport properties ($S$ and $\sigma$) coexistent with low thermal
conductivity ($\kappa$) are essential for achieving a high $zT$. However, sufficiently decoupling the
relationship between $S$, $\sigma$, and $\kappa$, which are linked by the carrier concentration, remains a
colossal challenge.$^{7,8}$

With an unsurpassed combination of room-temperature performance and device
processability, arguably, bismuth telluride, Bi$_2$Te$_3$, has been the outstanding representative in the
thermoelectric field for more than half a century.$^9$ As a basis material for chemical modification,
Bi₂Te₃ is extraordinarily flexible. Strategies such as energy filtering,¹⁰ band engineering¹¹ and doping,¹²,¹³ are among several that have been repeatedly demonstrated to improve the thermoelectric performance of Bi₂Te₃-based alloys. Moreover, the physical sensitivity of Bi₂Te₃ to different synthesis and processing routes (such as spark plasma sintering,¹⁴,¹⁵ self-propagating high-temperature synthesis,¹⁶,¹⁷ high-pressure sintering,¹⁸,¹⁹ etc.) has provided almost boundless opportunities to modulate crystal structure, texture, and microstructure from large single crystals to engineered nanoarchitectures.

Despite the many available options, most commonly the thermoelectric performance of Bi₂Te₃ is improved via substituting Sb for Bi and/or Se for Te, respectively.¹² Debatably, the success of these dopants has inhibited further extensive exploration of alternative chemical modifications in the Bi-Te system. This is perhaps surprising in that as yet there are no comparable n-type Bi₂Te₃ materials to match their Sb-doped p-type counterparts in terms of performance. This can be considered to be caused by two consequences. One of the reasons is known as the strong intrinsic electrical anisotropy in existing n-type Bi₂Te₃-based alloys,¹³,²⁰ leading to an unmanageable couple of the electron-phonon transport. Another one is the donor-like effect happened in n-type Bi₂Te₃,¹³,²¹ which readily gives rise to extremely high carrier concentration beyond the optimal range. The lack of a suitable n-type Bi₂Te₃ material has represented a bottleneck in the development of successful devices operating in the lower temperature regime.

Here, we introduce a new approach to tackling such bottlenecks in thermoelectric device development. We have employed a niobium dopant as a new approach to introduce negative charge carriers into the Bi-Te system. Bismuth niobium tellurides, (Bi,Nb)₂Te₃, have been successfully prepared by ball milling and high-pressure sintering. Progressive substitution of Nb for Bi has profound effects on crystallinity and microstructure. Moreover, the introduction of Nb
heteroatoms in Bi$_2$Te$_3$ clearly modulates both carrier concentration and carrier mobility. Multiple roles are performed by the dopant; Nb substitution boosts the electrical transport properties and thermoelectric performance. As a result, a maximum $zT$ of 0.94 has been achieved in n-type Bi$_{1.92}$Nb$_{0.08}$Te$_3$ at 505 K. Importantly, the action of Nb substitution that leads to electrical property enhancement has been elucidated. This knowledge will be beneficial when screening new donor atoms to improve the thermoelectric performance of n-type bismuth tellurides further.

2. EXPERIMENTAL DETAILS

2.1. **Materials synthesis.** Elemental Bi (Aladdin, 99.999%), Te (Aladdin, 99.999%), and Nb (Aladdin, 99.95%) powders were weighed and mixed in molar ratios corresponding to the chemical compositions of Bi$_{2-x}$Nb$_x$Te$_3$ ($x = 0, 0.06, 0.08,$ and 0.1). The mixtures were loaded into a steel milling jar (100 ml) in a recirculating glove box (Etelux Lab2000) under an N$_2$ atmosphere (O$_2$ and H$_2$O, ≤ 0.5 ppm). Each sample was subjected to high-energy ball milling (MSK-SFM-3 high speed rotating ball mill) using stainless steel balls in a ball:powder ratio of 5:1 by mass at 1200 rpm for 3 h. Each milled Bi$_{2-x}$Nb$_x$Te$_3$ sample was cold-pressed to form a φ 10.5 × 12 mm cylinder and inserted into the sample chamber of a high-pressure cubic anvil press (SPD 6 × 1200) for sintering in situ. The integrated heating cell rapidly subjected samples to a temperature of 693 K, while they were held under an applied pressure of 2 GPa for 10 min. The applied pressure was inferred following the calibration of changes in resistance of standard substances, and the temperature was measured using a Pt30 Rh/Pt6 Rh thermocouple junction placed near the sample. The as-prepared samples were polished and cut prior to further characterization.

2.2. **Materials characterization.** Crystal structures and phase compositions of the as-prepared sample pellets were determined by powder X-ray diffraction (XRD) using a Rigaku Ultima IV
X-ray diffractometer in Bragg-Brentano geometry with Cu-Kα radiation. Data were collected between 10-80° 2θ. Field-emission scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (FESEM-EDS; JEOL JSM-6701F microscope equipped with an Oxford X-Max spectrometer) and high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2100FS microscope and FEI, G2 F20X-Twin FEG microscope equipped with RTEM model SN9577 EDS spectrometer) were performed to image the samples across different length scales and to determine the spatially-resolved elemental composition. In the former case, samples were cut along the long axis (height; 12mm) of a cylindrical pellet (as depicted in Figure S1(a)) and each longitudinal cross-sectional sample was secured on an adhesive carbon tab attached to an aluminium sample stub. Samples for HRTEM, however, were prepared by grinding the pellets and dispersing the resulting powder in either ethanol or acetone (by sonication). The dispersion was dropped onto a copper sample grid and dried before analysis (see SI for further information). X-ray photoelectron spectroscopy (XPS) measurements were performed in UHV system at the base pressure ≤ 2·10^{-10} mbar using a Quantera SXM spectrometer (PHI, Japan) equipped with an Al-Kα excitation source. The room temperature carrier concentration (n) and mobility (μ) were determined using an ET9103-HS Hall measurement system. In addition, the electrical properties (S and σ) were measured in a helium atmosphere by a Nambro-3LT thermoelectric test system (JouleYacht, China). The thermal conductivity (κ) was measured by way of the thermal diffusivity using a Linseis LFA PT 1000 laser flash analyzer. The value of κ was calculated by using the equation, \( \kappa = \lambda C_p D \), where \( \lambda \), \( C_p \), and \( D \) are the thermal diffusivity, the specific heat capacity, and the relative density, respectively. The specific heat capacity, \( C_p \), was calculated from differential scanning calorimetry (DSC) data using a Linseis PT-1750 Simultaneous Thermal Analyzer, and the density, \( D \), was determined by the Archimedes method. Note that all
the thermoelectric quantities above were measured along the long axis direction of the pellet (12mm) in this work, using compact samples taken from the pellet as shown in Figure S1(b).

3. RESULTS AND DISCUSSION

XRD patterns of the as-prepared Bi$_{2-x}$Nb$_x$Te$_3$ sample pellets for $x = 0, 0.06, 0.08$, and $0.1$ are shown in Figure 1(a). In each case, all the diffraction peaks can be indexed to the characteristic Bragg reflections of the rhombohedral Bi$_2$Te$_3$ phase (PDF#15-863; Space group $R-3m$), no other crystalline phases could be detected. Preferred orientation is sometimes reported for polycrystalline Bi$_2$Te$_3$ samples given the high anisotropy of the unit cell and the predominant associated crystallite morphology. No such texturing effects are seen for the samples here, which can be attributed to the synthesis/processing route and principally the effect of ball milling on the particle shape and size. The lattice parameters of the samples as a function of niobium content can be estimated from the XRD data taken directly from the pellets using the positions of the (015) and (110) peaks and these are plotted in Figure 1(b). This semi-quantitative treatment indicates a reduction in $a$ and $c$ on initially introducing Nb ($0 < x \leq 0.08$) into the system. This result can be attributed to the Nb (1.45 Å) with a smaller atomic radius substituting for the Bi (1.60 Å) sites. A slight increase in lattice parameters is observed following further Nb content rise from $x = 0.08$ to $x = 0.1$. The abnormal tendency is considered as Nb doping content ($x = 0.1$) beyond the solubility limit of Nb in Bi$_2$Te$_3$ system, leading to local Nb that is not incorporated in the Bi lattices. Nevertheless, the content of unoccupied Nb is too less to reach the accuracy range of XRD detector, thus observing a single phase in the XRD pattern of Bi$_{1.9}$Nb$_{0.1}$Te$_3$ sample. Overall, the change of lattice parameters ($a$, $c$) with Nb content further suggests that low concentration of Nb ($x < 0.1$) has been successfully incorporated into Bi$_2$Te$_3$ structure via substituting for Bi.
Figure 1. (a) XRD patterns of as-prepared Bi$_{2-x}$Nb$_x$Te$_3$ sample pellets with $x = 0, 0.06, 0.08, \text{ and } 0.1$; (b) Plots of lattice parameters ($a$ and $c$) of the samples as a function of the Nb doping content, $x$ in Bi$_{2-x}$Nb$_x$Te$_3$ (as extracted from XRD data).

FESEM images for the samples are displayed in Figure 2. It is immediately noticeable that the texture of the Nb-doped samples is starkly different from that of Bi$_2$Te$_3$ itself; this despite the same synthesis and processing protocol having been applied to each sample. The contrast is even greater when compared to Bi$_2$Te$_3$ prepared only by high-pressure sintering (i.e. without milling; Figure S2(a)). The grains of bismuth telluride in Figure 2(a) exhibit an almost melt-like behavior where small (sub-micron sized) individual platelet particles have fused together to form a well-sintered, dense solid. By comparison, the microstructures of the niobium-containing samples, Bi$_{2-x}$Nb$_x$Te$_3$, are revealed to consist of particles that appear to be more discrete and the plate-like crystallites are less uniform than in Bi$_2$Te$_3$. Although there is evidence of sintering, the images suggest that no equivalent fusing process occurs in the Nb-doped samples (Figure 2(b)-(d)). Therefore, although the surfaces of the cleaved Nb-containing pellets are not as homogeneous as that seen in Bi$_2$Te$_3$, there remains a tendency for the pseudo-lamellar crystallites to align. The particle size distributions generated from the FESEM images (Figure 2(a)-(d) insets) show that the mean particle sizes of Bi$_{2-x}$Nb$_x$Te$_3$ are somewhat larger than that of Bi$_2$Te$_3$ itself (Figure 2(a)).
with an apparent maximum size at $x = 0.06$, although conversely, the matrices of the doped samples appear more porous. The results suggest that small quantities of niobium would appear to act so as to enhance the growth of the individual telluride crystallites. Meanwhile, FESEM image of the fracture surface in different directions has also been performed, as shown in Figure S2(b), which exhibits a similar texture due to the effect of ball milling process. In light of the evolving microstructure of the samples, one might expect: (a) that doping creates more sharply defined boundaries in the microstructure, which could impact on phonon scattering and decrease thermal conductivity$^{22}$ and (b) the less plate-like Nb-containing crystallites and their more random arrangements might reduce the anisotropy of the transport properties.

![Figure 2](image_url)

**Figure 2.** FESEM images of the fracture surfaces from pellets of as-prepared Bi$_{12-x}$Nb$_x$Te$_3$ with: (a) $x = 0$; (b) $x = 0.06$; (c) $x = 0.08$ and (d) $x = 0.1$. The inset plots in (a)-(d) represent the statistical particle size distributions for each respective sample.
Figure 3(a) shows the variation in the Seebeck coefficient as a function of temperature for the Bi$_{2-x}$Nb$_x$Te$_3$ samples. The negative Seebeck coefficient reveals n-type semiconducting behavior for all of the tellurides. The temperature dependence of the doped samples is rather similar with each exhibiting a decrease in the Seebeck coefficient (i.e. $S$ becomes increasingly negative) with increasing temperature until a minimum is reached at ca. 500 K. The values of $S$ then show a gentle increase thereafter. The changes in the Seebeck coefficient for Bi$_2$Te$_3$ itself are rather different, particularly at higher temperature, where the rate of change is steeper than in the doped materials. Moreover, the magnitude of $S$ is greater (more negative) below ca. 500 K for the $x = 0$ material, than for the Nb-doped samples. The observed behavior of the Bi$_2$Te$_3$ sample is consistent with previous knowledge that attributes the high (negative) Seebeck coefficient to the limited number of charge carriers; this situation changes dramatically at higher temperature (> 500 K) when the carrier concentration in Bi$_2$Te$_3$ increases dramatically due to thermal excitation. As shown in Figure 3(b), the electrical conductivity of the Nb-doped samples decreases slightly and almost linearly with increasing temperature until approximately 475 K at which point that rate of change in $\sigma$ with $T$ becomes greater. The electrical conductivity of Bi$_2$Te$_3$ also decreases with temperature, but at a more constant rate over the entire temperature range and the $x = 0$ sample remains the least conductive at all the temperatures measured. Hence doping with Nb improves the electrical conductivity of bismuth telluride with the highest conductivity for a composition of $x = 0.08$. Nevertheless, the $\sigma$ vs. $T$ profiles are broadly similar for all the telluride samples and exhibit behavior approaching that of a semimetal or a degenerate semiconductor. 

Consideration of the changes in thermal conductivity with temperature reveals some interesting trends among the Bi$_2$$_x$Nb$_x$Te$_3$ samples (Figure 3(c)). First, the replacement of bismuth
by niobium has profound effects on $\kappa$ and there is a clear trend of decreasing thermal conductivity with increasing niobium content. There is also a progressive deviation from the temperature dependency shown by $\text{Bi}_2\text{Te}_3$ ($x = 0$) with increasing $x$. The $\kappa$ vs. $T$ plot for bismuth telluride itself describes a shallow minimum at ca. 425 K. For $x > 0$, the profile changes from near temperature-independence ($x = 0.06$) to almost linear decreases in $\kappa$ with increasing temperature ($x = 0.08, 0.1$). For further investigation, the lattice thermal conductivity of the samples was calculated from total thermal conductivity subtracting electronic thermal conductivity, as shown in Figure S3. The results suggest that the lattice thermal conductivity exhibits a similar tendency as well as total thermal conductivity (Figure 3(c)), that is, the lattice thermal conductivity decreases significantly with increasing Nb content. The $\text{Bi}_{2-x}\text{Nb}_x\text{Te}_3$ sample with $x = 0.08$ possesses the ultralow lattice thermal conductivity compared with that of other samples over the measured temperature range. These observations above were considered as potentially attributable to changes in defect structure and carrier concentration as induced by Nb doping and these premises were investigated further as discussed below.

Overall, it is apparent that the enhanced electrical conductivity engendered by Nb doping is sufficient to overcome the concomitant drop in the magnitude of the (negative) Seebeck coefficient across all temperatures as compared to $\text{Bi}_2\text{Te}_3$. This effect can be clearly seen when considering the behavior of the power factor ($S^2\sigma$) as a function of temperature and composition in the $\text{Bi}_{2-x}\text{Nb}_x\text{Te}_3$ system (Figure S4). Coupled with the beneficial effects of doping on reducing the thermal conductivity, the net effect is to increase the value of $zT$ in the doped samples vs. $\text{Bi}_2\text{Te}_3$ itself across the entire temperature range (Figure 3(d)). The $zT$ vs $T$ plots represent a series of curves with a maximum that shifts slightly to higher temperature as a result of doping and the figure of merit themselves notably improve when Nb is introduced. A maximum $zT$ value of 0.94
is achieved in n-type Bi$_{1.92}$Nb$_{0.08}$Te$_3$ at 505 K, which significantly outperforms the sample of Bi$_2$Te$_3$ at all temperatures and also conspicuously surpasses the achievements of the other doped samples. Substituting niobium is thus evidently a successful way to improve n-type Bi$_2$Te$_3$ with an optimum composition, according to these results, realized at $x = 0.08$.

**Figure 3.** Temperature dependence of (a) the Seebeck coefficient; (b) the electrical conductivity; (c) the thermal conductivity and (d) the figure of merit, $zT$ for Bi$_{2-x}$Nb$_x$Te$_3$ ($x = 0, 0.06, 0.08, 0.1$).

In order to understand how the doping of niobium might impact on the microstructure of the system, the optimized Bi$_{1.92}$Nb$_{0.08}$Te$_3$ material was studied in detail by HRTEM. Selected resulting images are displayed in Figure 4. The image in Figure 4(a) clearly demonstrates the regular appearance of lattice fringes throughout the sample. The separation of these was
measured at 1.13(3) nm, which corresponds to the typical quintuple (Te(1)-Bi-Te(2)-Bi-Te(1)) layer spacing in the rhombohedral Bi$_2$Te$_3$-type structure. An enlarged view corresponding to the marked lattice fringes is shown in the circular inset of Figure 4(a), which clarifies the position of the quintuple layers by superimposing the idealized Bi$_2$Te$_3$ structure onto the HRTEM image. Meanwhile, EDS measurements performed by TEM on a single particle from a dispersed sample of the x = 0.08 composition are shown in Figure S5. The results exhibit a similar elemental ratio compared with the chemical composition of Bi$_{1.92}$Nb$_{0.08}$Te$_3$ sample, which supports the premise that Nb substitutes for Bi at an atomic scale within the Bi$_2$Te$_3$ crystal structure. According to the EDS spectrum in Figure S5, the Te content is lower than expected, implying a low level of Te-deficiency, which might be quantified in the x=0.08 samples as Bi$_{1.92}$Nb$_{0.08}$Te$_3$-$\delta$. Figure 4(b) shows an atomic resolution high magnification HRTEM image of a region of the Bi$_{1.92}$Nb$_{0.08}$Te$_3$-$\delta$ sample. The arrangement of atoms within the planes is clearly delineated and is highlighted in the top right inset in Figure 4b. This section corresponds to a magnified subsection of the image within the highlighted square (dashed yellow line) in the main figure and emphasizes the hexagonal arrangement of the atoms within the $ab$ plane of the Bi$_2$Te$_3$-type structure. A fast Fourier transform (FFT) image treatment for the highlighted area yields a diffraction pattern, which can be indexed in the [001] zone axis to the Bi$_2$Te$_3$ structure type (bottom left inset, Figure 4(b)). The combination of analytical and structural data from FESEM and HRTEM thus support the premise that the Nb heteroatoms doped into Bi$_2$Te$_3$ are incorporated within the telluride crystal structure itself, likely substituting for Bi within the lattice.
**Figure 4.** HRTEM images taken from Bi$_{1.92}$Nb$_{0.08}$Te$_3$ showing: (a) the quintuple Bi(Nb)-Te layers and their spacings within the rhombohedral Bi$_2$Te$_3$-type structure; the inset image shows an enlarged view of the quintuple layer structure with an idealized structural model superimposed (red and blue spheres represent Te and Bi(Nb) ions, respectively; (b) a high magnification-high resolution image of the sample, indicating the (-120) (-210) and (110) planes and their respective spacings. Both inset images are taken from the region defined by the yellow square in the main figure; the top right inset shows the hexagonal atomic arrangement of (Bi,Nb) (or Te) atoms within the $ab$ plane, whereas the bottom left inset shows the equivalent Fast Fourier Transform (FFT) image taken from the same region.

Further careful examination of multiple HRTEM images taken of the Bi$_{1.92}$Nb$_{0.08}$Te$_3$ sample provides additional insight into the microstructure of the Nb-doped telluride. The images shown in Figure 5 reveal multiple defects within the myriad of Bi-Nb-Te crystallites. A predominant lattice plane spacing of 3.23 Å can be readily measured across samples, as shown in Figure 5(a), which can be attributed to the characteristic (015) planes in the rhombohedral Bi$_2$Te$_3$ structure. This can be confirmed from the diffraction pattern generated in the FFT image in the inset. Within the same image, the rectangular marked region (yellow dashed line in Figure 5(a)) indicates a part of the crystallite rich in dislocations. This is confirmed when taking the inverse FFT (IFFT) image from within this area that is shown separately in Figure 5(b). The white
markers indicate some of the abundant dislocations. This is almost certainly a consequence of the lattice mismatch instigated by the substitution of Nb given the contrasting atomic radii of the Nb (1.45 Å) and Bi (1.60 Å) atoms.\textsuperscript{28}

Figure 5(c) reveals that individual grains with coherent grain boundaries can be readily discerned within discrete telluride crystallites. The observed nanoscale grains could be initially produced during the ball milling process and subsequently densified and “inherited” by the bulk material following high-pressure sintering, creating numerous grain boundaries within particles. Figure 5(d) demonstrates that the imperfections in the crystallites are not limited to extended defects. While the larger white ovoid regions in Figure 5(d) delineate extensive dislocations within the lattice, the smaller yellow circles indicate the location of apparent point defects within the sample. The formation of such point defects can be mainly attributed to the increased ionicity of the materials incurred by substitution of Nb and the affiliated loss of Te (by volatilization and possibly also incurred by ball milling).\textsuperscript{29,30} As is well known, the Pauling electronegativity of Nb (~1.6) is much lower than that of Bi (~2.02), meaning that the ionicity of the Nb-Te bonds will increase compared to that of the Bi-Te bonds. Aliovalent substitution in the increasingly ionic solid motivates the formation of point defects and more specifically the generation of vacancies at the tellurium sites, i.e. $V_{Te}^{\cdot\cdot}$. The emergence of such $V_{Te}^{\cdot\cdot}$ vacancies is of overall benefit to the system since the defects act as donor-like dopants not only potentially scattering phonons, but also providing 2 electrons per $V_{Te}^{\cdot\cdot}$ to modulate the carrier concentration in the solid.\textsuperscript{31} The anion vacancies therefore provide a route to enhance both the electrical and thermal properties of the doped tellurides complementing the role played by the plentiful dislocations in the layered structure, which are well known to contribute to phonon scattering.\textsuperscript{31} Imaging therefore demonstrates that Nb-doped Bi$_2$Te$_3$ possesses positive microstructural traits across multiple
length scales (such as micro- and nanoscale grains, dislocations, grain boundaries, and point defects) which can collectively restrict the transport of phonons over a breadth of frequencies.\textsuperscript{32} It is these factors that are likely to be primarily responsible for the significant reduction in the thermal conductivity of doped (Bi,Nb)\textsubscript{2}Te\textsubscript{3} materials as compared to bismuth telluride itself.

![Figure 5. HRTEM images taken from multiple crystallites in the Bi\textsubscript{1.92}Nb\textsubscript{0.08}Te\textsubscript{3-\delta} sample, which illustrate the predominance of both point and extended defects: (a) High magnification image of a single crystallite containing ordered and defective regions. The (015) planes are clearly visible in the former (with the corresponding FFT image shown in the inset) while dislocations are evident in the latter; (b) Inverse FFT image taken from within the rectangular highlighted region designated in (a). The markers indicate the...](image-url)
dislocations; (c) Coherent grain boundaries between adjacent nanoscale grains; (d) A selected area of the material illustrating abundant point defects (small yellow circles) and dislocations (larger white ellipses).

Having established the likely reasons for the reduction of thermal conductivity in the niobium-containing tellurides, it was important to try to assess the effects of doping on the electrical transport properties in the Bi-Nb-Te system more fully. The room-temperature carrier concentrations and mobilities as a function of niobium content, \( x \), for the Bi\(_{2x}\)Nb\(_x\)Te\(_{3-\delta}\) samples are displayed in Figure 6(a). As \( x \) is increased, the carrier concentration exhibits parabolic-like behavior, reaching a maximum close to \( x = 0.06 \). Simultaneously, the carrier mobility follows an almost inverse behavior with Nb content, \( x \), with a minimum in the mobility also at \( x = 0.06 \). It is vital to appreciate the valence state of the niobium dopant when interpreting these phenomena. We performed XPS measurements in an attempt to clarify this situation and to ascertain the origin of the doped electrons. From these experiments, it is evident that the doped Nb species mainly exist in three different oxidation states (Figure S6(a)). The triple peaks observed at 203.87, 206.73, and 210.20 eV correspond to the Nb\(^{+2}\) 3d\(_{5/2}\), Nb\(^{+4}\) 3d\(_{3/2}\), and Nb\(^{+5}\) 3d\(_{3/2}\) transitions respectively.\(^{33-35}\) The Nb\(^{+5}\) 3d\(_{5/2}\) transition can be tentatively identified at 208.25 eV, but the remaining Nb transitions are not detected. The relative amount of each Nb species is shown in Table S1. The higher niobium oxidation states as manifested by Nb\(^{+4}\) and Nb\(^{+5}\) peaks in the XPS spectrum,\(^{36-38}\) commonly occur from the formation of oxides (and therefore Nb-O bonds) due to adventitious oxygen introduced during the high-pressure sintering process. This premise is corroborated by the form of the Bi peaks in the XPS spectra (Figure S6(b)) which indicate lesser, but still significant, contributions to the Bi\(^{3+}\) 4f\(_{7/2}\) and Bi\(^{3+}\) 4f\(_{5/2}\) transitions from the ions in an oxide environment (i.e. Bi-O bonds). The Te 3d peaks can be attributed to the Te\(^{2-}\) 3d\(_{5/2}\) and Te\(^{2-}\) 3d\(_{3/2}\) transitions, consistent with Te(-II) in the (Bi\(_x\)Nb\(_y\))\(_2\)Te\(_3\) system (Figure S6(c)). These
observations suggest some degree of oxidation at the sample surface that likely occurs during sample processing (e.g. high-pressure sintering). The clear presence of Nb(II) in the XPS spectra (as indicated by the Nb$^{2+}$ 3d_{5/2} peak) is very interesting. If one assumes that Nb is integrated into the Bi$_2$Te$_3$ phase and that the aliovalent Nb$^{3+}$/Bi$^{3+}$ substitution occurs, then the incorporation of niobium cations would introduce electrons to increase the carrier concentration in n-type Nb-substituted Bi$_2$Te$_3$. Moreover, if tellurium vacancies, $V_{Te}^{\ddagger}$, are formed as a result of Nb doping (i.e. Bi$_{2-x}$Nb$_x$Te$_{3-\delta}$) then this provides a route to increased carrier concentration as has been elaborated above.

The Nb donors thus perform multiple roles: first, increasing carrier concentration, which contributes to a significant increase in the electrical conductivity and second, restricting the effects of bipolar thermal conduction, reducing $\kappa$, particularly at higher temperatures (as shown in Figure 3(c)). However, as was also evident from Figure 6(a), the carrier mobility decreases in the Bi$_{2-x}$Nb$_x$Te$_{3-\delta}$ tellurides as the Nb doping level increases. This is not altogether surprising as it is well known that lattice mismatch defects induced by heteroatom doping, such as the dislocations observed in this Bi-Nb-Te system, can lead to an increase of carrier (electron) scattering.$^{39,40}$ From a chemical bonding perspective, replacement of Bi (with a Pauling electronegativity of $\chi \approx 2.02$) by less electronegative Nb ($\chi \approx 1.6$) results in higher ionicity Nb-Te bonds.$^{28,41}$ The lower covalency of the Nb-Te vs. the Bi-Te bonds can give rise to a decrease in carrier mobility as electrons become more localised.$^{42}$

Finally, one needs to consider the effect of Nb doping on the Seebeck coefficient in more detail. Figure 6(b) shows the carrier concentration dependence of the Seebeck coefficient (as given by the Pisarenko relation). From this, one can evaluate the effect of replacing Bi by Nb on the density of states effective mass ($m^*$) of the Bi$_{2-x}$Nb$_x$Te$_{3-\delta}$ materials. The Pisarenko relation is
described in terms of the following equation (1) according to a single parabolic band (SPB) model:\textsuperscript{43,44}

$$S = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* \left( \frac{\pi}{3n} \right)^{2/3}$$  \hspace{1cm} (1)

where $S$ is the Seebeck coefficient, $T$ is the absolute temperature, $n$ is the carrier (electron) concentration and $k_B$, $e$, and $h$ are the Boltzmann constant, the elementary charge, and the Planck constant, respectively. The result indicates that the effective mass of the Bi$_{2-x}$Nb$_x$Te$_{3-\delta}$ compounds increases with Nb doping and is concentrated in a small range of $m^*$ values from $1.08m_e$ to $1.47m_e$ for $x \neq 0$ (where $m_e$ is the mass of an electron, $9.11 \times 10^{-31}$ kg). These results suggest that the fluctuation of the Seebeck coefficient seen in the Nb-doped samples is mainly influenced by carrier concentration. However, the influence of Nb doping on the effective mass, $m^*$ in the Bi$_2$Te$_3$ system also has adverse effects on carrier mobility given the inversely proportional relationship, $\mu \propto 1/m^*$. In order to evaluate the influence of various substituents at the Bi sites in doped Bi$_2$Te$_3$ as compared with niobium, selected literature data from Bi$_2$Te$_3$ materials in which only substitutions were made for Bi have been annotated in the plot in Figure 6(b) (as indicated by the ellipse defined by the blue dotted line).\textsuperscript{45-51} Interestingly, all these data are clustered within a region based around the $m^* = 1.08$-$1.47m_e$ curves in the Pisarenko plot. This finding is important in understanding the multiple roles of the niobium dopant in moderating the electronic properties of the Bi$_{2-x}$Nb$_x$Te$_{3-\delta}$ materials. Nb substitution for Bi clearly increases the carrier concentration such that for $0.06 \leq x \leq 0.1$ the value of $n$ exceeds those in other substituted bismuth tellurides of similar effective mass by an order of magnitude or more. The significance of this is that despite the net decrease in the Seebeck coefficient as a result of substitution, the improvement in electrical conductivity is always comparatively greater in terms of its influence on the power factor. Combined with the favorable effects on the thermal conductivity achieved
across length scales, niobium substitution has been proven to be a powerful tool in enhancing the value of $zT$ in n-type bismuth telluride and could be an applicable strategy across a far wider range of low- to mid-temperature regime thermoelectrics. Such an approach combined with nanoscaling methodologies previously shown to be effective for Bi$_2$Te$_3$,\textsuperscript{52} is an aspect of our continuing research.

**Figure 6.** (a) Plots of carrier concentration (black) and carrier mobility (blue) measured at 300 K as functions of the Nb doping content, $x$ in Bi$_{2-x}$Nb$_x$Te$_3$; (b) Room-temperature Hall carrier concentration dependence of the Seebeck coefficient (Pisarenko relation) for the Bi$_{2-x}$Nb$_x$Te$_3$ ($0 \leq x \leq 0.1$) materials. The datapoints within the blue dotted ellipse are taken from literature reports\textsuperscript{45-51} of materials in which only Bi site-substitution occurs in Bi$_2$Te$_3$.

**4. CONCLUSIONS**

In summary, we have demonstrated the feasibility of employing niobium as a highly effective new dopant to introduce electrons into bismuth telluride. The transition metal dopant has a dramatic effect on the thermoelectric performance of the materials, with a maximum $zT$ of 0.94 achieved in n-type Bi$_{1.92}$Nb$_{0.08}$Te$_{3-\delta}$ at 505 K. Results suggest that Nb heteroatoms substitute for Bi at the metal sites and exhibit multiple roles in the tuning of carrier concentration and mobility, improving the electrical transport properties of the substituted materials compared to Bi$_2$Te$_3$. 
itself. Simultaneously, the introduction of Nb induces both extended defects (dislocations) and point defects (tellurium vacancies), modulating carrier scattering and impeding the transport of phonons, effectively decreasing the thermal conductivity. This study provides a new perspective in the deployment of non-routine dopants such as 4d transition metals in chalcogenide thermoelectrics. The work suggests that such unconventional “multirole” donors could provide an intriguing and highly rewarding track towards new n-type thermoelectrics.

ASSOCIATED CONTENT

Supporting Information.

Schematic diagrams of sample cutting for measurements (Figure S1), FESEM image (Figure S2), lattice thermal conductivity (Figure S3), power factor (Figure S4), TEM-EDS spectrum (Figure S5), XPS spectra (Figure S6), and the relative amount of the observed Nb species (Table S1).

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Notes

The authors declare no competing financial interest.

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