Published in final edited form as:

Chem Mater. 2019 June 25; 31(12): 4460–4468. doi:10.1021/acs.chemmater.9b00964.

Synthesis and characterization of vacancy-doped neodymium telluride for thermoelectric applications

Steven J. Gomez^{1,2,†}, Dean Cheikh^{1,†}, Trinh Vo¹, Paul Von Allmen¹, Kathleen Lee¹, Max Wood³, G. Jeff Snyder³, Bruce S. Dunn², Jean-Pierre Fleurial¹, Sabah K. Bux^{1,*}

¹Thermal Energy Conversion Technologies Research and Advancement Group, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109-8099

²Department of Materials Science and Engineering, University of California, Los Angeles 90092

³Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

Abstract

Thermoelectric materials exhibit a voltage under an applied thermal gradient and are the heart of radioisotope thermoelectric generators (RTGs), which are the main power system for space missions such as *Voyager I*, *Voyager II*, and the Mars *Curiosity* rover. However, materials currently in use enable only modest thermal-to-electrical conversion efficiencies near 6.5% at the system level, warranting the development of material systems with improved thermoelectric performance. Previous work has demonstrated large thermoelectric figures of merit for lanthanum telluride ($\text{La}_{3-x}\text{Te}_4$), a high-temperature *n*-type material, achieving a peak zT value of 1.1 at 1275 K at an optimum cation vacancy concentration. Here we present an investigation of the thermoelectric properties of neodymium telluride ($\text{Nd}_{3-x}\text{Te}_4$), another rare-earth telluride with a similar structure to $\text{La}_{3-x}\text{Te}_4$. Density functional theory (DFT) calculations predicted a significant increase in the Seebeck coefficient over $\text{La}_{3-x}\text{Te}_4$ at equivalent vacancy concentrations due to an increased density of states (DOS) near the Fermi level from the 4f electrons of Nd. The high temperature electrical resistivity, Seebeck coefficient, and thermal conductivity were measured for $\text{Nd}_{3-x}\text{Te}_4$ at various carrier concentrations. These measurements were compared to $\text{La}_{3-x}\text{Te}_4$ in order to elucidate the impact of the four 4f electrons of Nd on the transport properties of $\text{Nd}_{3-x}\text{Te}_4$. A zT of 1.2 was achieved at 1273 K for $\text{Nd}_{2.78}\text{Te}_4$, which is a 10% improvement over that of $\text{La}_{2.74}\text{Te}_4$.

GRAPHICAL ABSTRACT

*Corresponding Author Sabah K. Bux, Sabah.K.Bux@jpl.nasa.gov.

†These authors contributed equally to this work.

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

Supporting Information. Sample porosities, scanning electron micrographs, X-ray diffraction patterns of ball-milled powder, temperature-dependent carrier concentrations, Seebeck vs. resistivity at 600 K, thermal diffusivity vs. temperature, heat capacity measurements, refined compositions, refined lattice parameters.

INTRODUCTION

Radioisotope thermoelectric generators (RTGs) have been a key enabling technology for the National Aeronautics and Space Administration (NASA) to power deep-space exploration vehicles. These generators utilize thermoelectric materials to convert heat from the spontaneous decay of a radioisotope into electrical energy, providing power to the spacecraft. Since thermoelectrics are solid-state devices, the nature of RTGs has allowed them to demonstrate long-term reliability, as evidenced by the *Voyager* I and II missions, which have been continuously operating for over 40 years.^{1,2} Although RTGs are robust and highly dependable, state-of-the-art RTGs utilize heritage thermoelectric materials (Si-Ge alloys, PbTe, and Te-Ag-Ge-Sb) which exhibit only modest thermal-to-electrical beginning-of-life conversion efficiencies of approximately 6.5% at the system level.³ These conversion efficiencies are limited by the low average values of the dimensionless figures of merit (zT) of the state-of-the-art materials across their operating temperature ranges.^{3–6} zT is defined as $zT = S^2 T / \rho \kappa$ and high performance materials will possess a large Seebeck coefficient (S), low electrical resistivity (ρ), and low thermal conductivity (κ). Furthermore, since the efficiency of a RTG is dependent on the temperature gradient across the thermoelectric material, T , materials with higher operating temperatures are of interest as well. Identification of new materials with high zT 's and with high melting points are desirable to potentially increase the specific power of RTGs (W/kg), which could allow for more scientific instrumentation on a spacecraft while also reducing the amount of radioisotope heat-source fuel required for a specific power output.^{7,8}

Lanthanum telluride ($\text{La}_{3-x}\text{Te}_4$) has been identified as a high-temperature, n -type thermoelectric material.^{3,8,9} $\text{La}_{3-x}\text{Te}_4$ adopts the Th_3P_4 structure type ($I\bar{4}3d$) with 28 atoms per unit cell, and this structure allows for La^{3+} vacancy concentrations of up to $x = 0.33$.^{8,9} The carrier concentration of $\text{La}_{3-x}\text{Te}_4$ is controlled by these La^{3+} vacancies, as each lanthanum atom contributes 3 electrons, and each tellurium atom accepts 2 electrons. With no vacancies ($x = 0$, La_3Te_4) there is one free electron per formula unit, and metallic behavior is observed. With the maximum vacancy concentration ($x = 0.33$, $\text{La}_{2.67}\text{Te}_4$), there are no free electrons present and it behaves as an insulator. Furthermore, $\text{La}_{3-x}\text{Te}_4$ possesses an intrinsically low lattice thermal conductivity (κ_L) resulting from the complex Th_3P_4 structure, phonon point-defect scattering from vacancies, and electron-phonon scattering at more metallic compositions. The combination of these favorable properties result in a high zT of 1.1 at 1273 K with an optimized stoichiometry of $x = 0.26$ ($\text{La}_{2.74}\text{Te}_4$).⁸ The excellent

electronic properties of $\text{La}_{3-x}\text{Te}_4$ stem from the large Seebeck coefficient that results from heavy conduction bands.¹⁰ Computational modeling has shown that the electronic density of states (DOS) of $\text{La}_{3-x}\text{Te}_4$ is controlled by the La states in the conduction band whereas the valence band states are dominated by the Te atoms.^{10–12} In the conduction band, a peak in the DOS near the Fermi level enables $\text{La}_{3-x}\text{Te}_4$ to maintain a high Seebeck coefficient at high carrier concentrations ($n \sim 0.9 \times 10^{21}$ when $x = 0.26$). Modifications of the conduction band states have been performed using divalent substitutions (Ca and Yb) on the La sites, but these were found to have little impact on zT .^{9,12} Inspection of the conduction band states shows that they are primarily composed of the La 5d states, with some contribution coming from the empty La 4f states. The limited contribution of the 4f states is a result of La having no 4f electrons. Recently, praseodymium telluride ($\text{Pr}_{3-x}\text{Te}_4$), another rare-earth telluride with the Th_3P_4 structure type, was investigated, and through band structure calculations it was found that the introduction of the three 4f electrons of Pr resulted in a significant shift of the peak in the DOS closer to the conduction band edge when compared to $\text{La}_{3-x}\text{Te}_4$.¹³ As a result, at equivalent vacancy concentrations, $\text{Pr}_{3-x}\text{Te}_4$ exhibited a 25% improvement in the Seebeck coefficient over $\text{La}_{3-x}\text{Te}_4$. This increase, coupled with a lower thermal conductivity, resulted in a $zT = 1.7$ at 1200 K for $\text{Pr}_{3-x}\text{Te}_4$. There exist many other Th_3P_4 structure type compounds. Many of these compounds have been previously investigated for high-temperature thermoelectric applications.^{5,14–20} However, they were synthesized via solid-state reaction or melting, often requiring temperatures over 2000 K.^{21–23} At such elevated temperatures, the large differences in melting points of tellurium (722 K) and the rare-earth elements (1208 K for praseodymium) would lead to vapor phase loss of tellurium, resulting in inhomogeneity in samples and poor stoichiometric control, making control of the carrier concentration challenging. To circumvent these issues, mechanochemical synthesis has been successfully used to synthesize both $\text{La}_{3-x}\text{Te}_4$ and $\text{Pr}_{3-x}\text{Te}_4$ at low temperatures, reproducibly forming compounds with precise stoichiometries.^{8,12,13} Here, we extend this technique to synthesize the compound neodymium telluride ($\text{Nd}_{3-x}\text{Te}_4$). The additional 4f electron of neodymium (four total) over praseodymium may further modify the conduction band states favorably and enhance the zT of the material. A series of $\text{Nd}_{3-x}\text{Te}_4$ samples were mechanochemically synthesized with varying vacancy concentrations and consolidated using spark plasma sintering (SPS). The samples were then characterized for phase purity and their thermoelectric properties measured to 1273 K.

RESULTS AND DISCUSSION

Electronic Structure

Band structure calculations are valuable tools to understand and better engineer complex thermoelectric materials. In the current work, we employed first principles calculations to observe the differences between the band structure and DOS of Nd_3Te_4 and La_3Te_4 . The primary difference between Nd and La is that Nd possesses four 4f electrons. Figure 1(A) shows a comparison of the DOS of La_3Te_4 and Nd_3Te_4 . Both compounds possess a sharp peak in the conduction band primarily composed of 4f states of the rare-earth cation. For La_3Te_4 , this peak is located approximately 1 eV above the Fermi level while the f peak for Nd_3Te_4 is situated at the Fermi level. The shift of the f peak of Nd_3Te_4 closer to the Fermi

energy is expected to impact the electrical transport properties and enhance the Seebeck coefficient.

Figure 1(B) and (C) show the calculated electronic band structure for La_3Te_4 and Nd_3Te_4 , respectively. In both cases, the conduction band edge is defined by the first two degenerate bands, and these two bands are expected to have the largest contribution to the transport properties. However, the remarkable difference between the two band structures lies in the location of the dense region of bands, to which the main contribution comes from the f states. While for La_3Te_4 , the majority of the bands are farther above the Fermi level and therefore have a very small contribution to transport, for Nd_3Te_4 this dense region has been shifted closer to the conduction band edge and is on top of the Fermi level. Due to the larger contribution of the f orbitals to the bands at the Fermi level, the band curvature at the H, N, and Γ points becomes smaller for Nd_3Te_4 , indicating that Nd_3Te_4 has an increased electron effective mass compared to La_3Te_4 .

The Seebeck coefficients for both materials were computed using standard expressions derived from the linearized Boltzmann Transport Equation and a rigid band approximation to describe the variation of electron concentration due to vacancies.^{10,24,25} Figure 1(D) compares the Seebeck coefficients of La_3Te_4 and Nd_3Te_4 as a function of carrier concentration at 1200 K. In the carrier concentration range of interest ($1.0 \times 10^{21} - 1.0 \times 10^{22} \text{ cm}^{-3}$), the Seebeck coefficient of Nd_3Te_4 is expected to be twice that of La_3Te_4 . This improvement agrees well with the predicted increase in the DOS near the Fermi level and suggests an improvement in total thermoelectric performance.

Sample Characterization

Structure.—Interestingly, the Nd-Te phase diagram, unlike that of $\text{La}_{3-x}\text{Te}_4$ and $\text{Pr}_{3-x}\text{Te}_4$, indicates that the orthorhombic Th_2S_3 structure type is favorable at temperatures below 1273 K, with a phase transition to the cubic Th_3P_4 structure above 1273 K.²⁶ For the metallic lower vacancy concentrations the crystal structure of the material was found to be the cubic Th_3P_4 crystal structure, as seen in Figure 2(A). The samples adopting the cubic Th_3P_4 structure type were shown to be phase pure by X-ray diffraction. The Th_3P_4 structure was observed for lower vacancy concentrations of $\text{Nd}_{3-x}\text{Te}_4$ even before any high temperature sintering, as shown in Figure S2. However, when samples are prepared near and at the Nd_2Te_3 composition, they are observed to have the orthorhombic Th_2S_3 structure as shown in Figure 3(A), suggesting that the increased number of vacancies in the structure leads to instability of the Th_3P_4 phase.

A 7-day annealing study on Nd_3Te_4 at 1173 K revealed no change in structure (Figure 3(B)) suggesting that the transition to the orthorhombic phase may be kinetically rate limited. A 4-day anneal of the Nd_2Te_3 composition at 1373 K demonstrated a phase transition from the Th_2S_3 structure type to the Th_3P_4 structure type (Figure 3(C)). However, due to the low carrier concentration, these samples were mechanically weak and broke apart when handled, preventing transport measurements from being made.

To further observe the phase homogeneity of the samples, a scanning electron microscope (SEM) was used to image the polished surfaces of sintered compacts (Figure 2(B), Figure

S1). From these images all samples were found to be homogenous, with only small amounts of residual porosity (less than 0.1%) from the compaction process. All of these sintered compacts possessed densities over 96% that of theoretical values (Table 1).

Composition.—The nominal compositions of the $\text{Nd}_{3-x}\text{Te}_4$ series are reported in Table 2 along with the measured composition determined by wavelength-dispersive X-ray spectroscopy (WDS) on sintered pellets. The measured composition is an average value of ten WDS measurements per composition. The measured compositions for lower vacancy concentration samples were in agreement with nominal compositions. However, higher vacancy concentration samples ($x > 0.15$) had systematically lower measured values of x , likely as a result of the error in the WDS measurement. Calculated carrier concentrations were obtained from WDS compositions and are plotted with measured Hall carrier concentrations in Figure 4(A), showing excellent agreement.

Electronic Transport Properties

To characterize the electronic properties of $\text{Nd}_{3-x}\text{Te}_4$, the Seebeck coefficient, electrical resistivity, carrier mobility, and carrier concentration were measured over the temperature range 300 K to 1273 K in vacuum (10^{-6} Torr). Figure 4(B) shows electrical resistivity as a function of temperature. The $\text{Nd}_{3-x}\text{Te}_4$ samples were found to exhibit typical heavily doped semiconductor-like behavior and are more resistive than $\text{La}_{3-x}\text{Te}_4$ for similar vacancy concentrations. Samples with lower carrier concentrations and higher vacancy concentration are more resistive, as expected.

It is well documented that a multi parabolic band model is needed to describe electronic transport in $\text{La}_{3-x}\text{Te}_4$.¹⁰ As expected from our computational results, we find similar behavior in $\text{Nd}_{3-x}\text{Te}_4$ with the Pisarenko plot (Fig 5(B)) being too flat to be described simply by a single parabolic band. At 300K, we experimentally find the transport in $\text{Nd}_{3-x}\text{Te}_4$ and $\text{La}_{3-x}\text{Te}_4$ to be remarkably similar such that the same model inputs can be used to describe both compounds. At elevated temperatures, we see a slight divergence in the properties of the two compounds with $\text{Nd}_{3-x}\text{Te}_4$ samples lying slightly higher than $\text{La}_{3-x}\text{Te}_4$ in the Pisarenko plot. This difference can be explained by heavy higher-energy bands, such as those created by the f-states, being lower in energy in $\text{Nd}_{3-x}\text{Te}_4$ than in $\text{La}_{3-x}\text{Te}_4$. In this case, it is possible that these states may not be activated until there is significant broadening of the Fermi-Dirac distribution at higher temperatures.

Figure 4(D) shows a change in the slope of the electron mobility near 850 K, likely due to the activation of a higher energy band from broadening of the Fermi-Dirac distribution. The temperature-dependent carrier concentration is shown in Figure S3.

The temperature-dependent Seebeck coefficient is shown in Figure 5(A). The Seebeck coefficient increases with increasing temperature, indicative of heavily doped semiconducting behavior. Higher vacancy concentration $\text{Nd}_{3-x}\text{Te}_4$ samples possess higher Seebeck coefficients relative to $\text{La}_{3-x}\text{Te}_4$ at similar vacancy concentrations. This increase is consistent with the predicted modifications to the band structure from the 4f electrons of Nd. The Seebeck coefficient increases with decreasing carrier concentration and agrees well with values predicted by SPB modeling shown in Figure 5(B). It should also be noted that, for

similar carrier concentrations, $\text{Nd}_{3-x}\text{Te}_4$ possesses a larger Seebeck coefficient than $\text{La}_{3-x}\text{Te}_4$ as predicted by DFT calculations. A plot of Seebeck vs. resistivity is shown in Figure S4. The temperature dependent power factor (S^2/ρ) is shown in Figure 5(D), and is similar at equivalent vacancy concentrations for both $\text{La}_{3-x}\text{Te}_4$ and $\text{Nd}_{3-x}\text{Te}_4$. This suggests that the improvements observed in the Seebeck coefficient are offset by the correspondingly higher resistivity of $\text{Nd}_{3-x}\text{Te}_4$.

Thermal Transport Properties

The thermal diffusivity (α) was measured (Figure S7) and the thermal conductivity (κ) was calculated using the measured heat capacity (Figure S8). The thermal conductivity of $\text{Nd}_{3-x}\text{Te}_4$ was found to be lower than that of $\text{La}_{3-x}\text{Te}_4$ for equivalent vacancy concentrations (Figure 6(A)). The total thermal conductivity is the sum of electronic (κ_e) and lattice (κ_L) contributions. The electronic contribution to the thermal conductivity was calculated using the Wiedemann-Franz law, $K_e = LT/\rho$, where L is the Lorenz number, and then subtracted from κ to calculate κ_L . A simplified variable Lorenz number was used, which was calculated as a function of Seebeck coefficient using the approximation $L = 1.5 + \exp(-|S|/116)$ and resulted in Lorenz numbers between 1.5 and $2.2 \times 10^{-21} \text{ W}\cdot\Omega\cdot\text{K}^{-2}$.²⁷ The lattice thermal conductivity shows little difference from that of $\text{La}_{3-x}\text{Te}_4$, as seen in Figure 6(B), indicating that the lower total thermal conductivity of $\text{Nd}_{3-x}\text{Te}_4$ is a result of its increased resistivity.

Thermoelectric Figure of Merit

Using these measurements, zT was calculated as a function of temperature and is shown in Figure 6(C). $\text{Nd}_{3-x}\text{Te}_4$ shows an improvement in zT compared to $\text{La}_{3-x}\text{Te}_4$ at similar vacancy concentrations due to a lower total thermal conductivity. The highest zT was achieved with the composition $\text{Nd}_{2.78}\text{Te}_4$ and reached 1.2 at 1273 K, representing a 10% improvement over $\text{La}_{2.74}\text{Te}_4$. Figure 6(D) shows zT as a function of carrier concentration at 600 K. Because $\text{La}_{3-x}\text{Te}_4$ and $\text{Pr}_{3-x}\text{Te}_4$ optimize at carrier concentrations near $1 \times 10^{21} \text{ cm}^{-3}$, a higher zT may be possible for $\text{Nd}_{3-x}\text{Te}_4$ at a lower carrier concentration.^{8,13} However, the Th_3P_4 structure in $\text{Nd}_{3-x}\text{Te}_4$ becomes unstable at the high vacancy concentrations necessary to reach these lower carrier concentrations and thus, synthesis of samples with lower carrier concentrations was not feasible.

CONCLUSIONS

We employed density functional theory to perform band structure calculations for Nd_3Te_4 and La_3Te_4 to compare the impact of the four 4f electrons of Nd to the transport properties of $\text{Nd}_{3-x}\text{Te}_4$, which predicted a sharp peak in the density of states situated near the Fermi level in Nd_3Te_4 . A higher Seebeck coefficient was predicted for Nd_3Te_4 when compared to La_3Te_4 , in agreement with the predicted increase in the DOS near the Fermi level. $\text{Nd}_{3-x}\text{Te}_4$ was synthesized over a range of vacancy concentrations, and was found to exhibit the metastable cubic Th_3P_4 structure type for lower vacancy concentrations after mechanochemical synthesis. Phase purity of the Th_3P_4 structure was confirmed via X-ray diffraction, and sample compositions were analyzed using wavelength dispersive X-ray spectroscopy. The electronic and thermal properties were measured, and $\text{Nd}_{3-x}\text{Te}_4$ was found to have a higher resistivity and higher Seebeck coefficient at equivalent vacancy

concentrations, as well as lower electronic contribution to thermal conductivity than $\text{La}_{3-x}\text{Te}_4$. With regard to thermoelectric performance, the increase in Seebeck coefficient was offset by a corresponding increase in resistivity.²⁸ However, this increased resistivity also served to lower the thermal conductivity. A $zT = 1.2$ was achieved at 1273 K for $\text{Nd}_{2.78}\text{Te}_4$, which is a 10% improvement over that of $\text{La}_{2.74}\text{Te}_4$. If used in future RTGs, $\text{Nd}_{3-x}\text{Te}_4$ will serve to increase the thermal-to-electrical conversion efficiencies in these devices, enabling higher specific power densities and reduced dependence on precious radioisotope fuel.

EXPERIMENTAL PROCEDURES

Band Structure Calculations

The structural relaxation and electronic properties of La_3Te_4 and Nd_3Te_4 were computed with the open source DFT software package Quantum Espresso (QE).²⁹ It is well known that the f states in rare-earth (RE) compounds are not adequately described by standard local density approximation (LDA) and generalized-gradient approximation (GGA) due to strong electronic correlation effects.^{30,31} To address this shortcoming, PBE plus on-site Coulomb interaction (PBE+U) was used in this work.^{32–34} The on-site Coulomb interaction serves to correct the self-interaction for the f electrons localized at the RE sites. Projected augmented wave (PAW) potentials generated with the AUTOPAW program were used for La and Nd with an energy cutoff of 50 Ry for the wave functions and a charge density cutoff of 450 Ry.^{35,36} Since Nd_3Te_4 and La_3Te_4 are metallic, the Mazari-Vanderbilt smearing scheme was used to expedite the convergence toward self-consistency.³⁷ Brillouin zone k -point sampling of $13 \times 13 \times 13$ and $19 \times 19 \times 19$ were used for the structural relaxation and transport property calculations (Seebeck coefficient), respectively. The choice of energy cutoff and k -points was from the details of convergence tests. La_3Te_4 and Nd_3Te_4 have the Th_3P_4 structure, belonging to the cubic crystal system and space group $I\bar{4}3d$.^{5,8} The atomic positions of both structures were relaxed for various fixed lattice parameters. The lattice parameter corresponding to the minimum total energy is found to be 9.70 Å for La_3Te_4 , in good agreement with the experimental values of 9.622 Å.⁸ For Nd_3Te_4 , we computed the lattice constant for several values of U. We found that $U = 3.1$ eV gives a relaxed lattice constant of 9.48 Å, in excellent agreement with the experimental value of 9.437 Å, with an error of ~0.5%.³⁸ At room or higher temperatures, both materials are paramagnetic. For this reason, we discuss the electronic properties of Nd_3Te_4 for non-spin polarized calculations, since it more closely describes the properties of Nd_3Te_4 at or above room temperature.

Multi-Band Modeling

Multi-band modeling used effective masses, degeneracies, and energy differences between bands reported by May et al. for $\text{La}_{3-x}\text{Te}_4$.¹⁰ The three bands involved in this model have masses of $m_1^* = 1.13 m_e$, $m_2^* = 1.05 m_e$, and $m_3^* = 1.56 m_e$, and degeneracies of $g_1 = 2$, $g_2 = 1$, and $g_3 = 2$. The 2nd band is offset in energy above the first set of bands by 0.30 eV, and the 3rd set of bands is offset in energy above the first set of bands by 0.33 eV. This semi-empirical model assumes deformation potential scattering, which is backed up experimentally by the temperature dependence of mobility. As in May et al., a constant relaxation time in each band is assumed in order to construct this model.¹⁰

Synthesis

All preparation steps were performed in an argon dry box. The $\text{Nd}_{3-x}\text{Te}_4$ samples were mechanochemically synthesized in a ball mill, using 99.9% Nd (Stanford Advanced Materials) and 99.999% Te (5N Plus Inc.) as precursors. The elements were combined in a stainless steel vial with stainless steel balls and milled in a SPEX SamplePrep 8000 for over 10 hours until homogeneous $\text{Nd}_{3-x}\text{Te}_4$ powders were synthesized. The powders were then loaded in to graphite dies and compacted using spark plasma sintering (SPS) at a pressure of 80 MPa and at temperatures above 1500 K. The Archimedes method was used to determine sample densities in toluene.

Characterization

X-ray diffraction measurements were carried out using a Bruker D8 Discover powder X-ray diffractometer using Cu K α radiation. Densified pellets were ground into powder using a mortar and pestle and an internal standard of 325 mesh Si powder (99.999%, Alfa Aesar) was added to the ground compacts. X-ray diffraction measurements for phase identification as shown in Figure 3(A) were performed on densified pellets. For Rietveld refinement, these sintered compacts were ground into powder in an argon glovebox, placed in an air-sensitive powder holder and sealed with a Kapton film before transferring to the diffractometer. The Kapton film produced two residual broad peaks at about 22° and 26° 2 θ as shown in Figure 2(A), even after subtracting the Kapton profile. Scans were performed over a 2 θ range of 20° to 80° using a step size of 0.0354094° and a dwell time of 1.5 seconds. Scanning electron microscopy was performed using a ZEISS 1550VP Field Emission SEM. Sample porosity was calculated using ImageJ by determining the area fraction of dark regions in the SEM images. Electron probe micro-analysis (EPMA) was performed using a JEOL JXA-8200 micro-analyzer with NdPO_4 and elemental Te as standards. The Seebeck coefficient was measured from 300 K to 1273 K using custom equipment using a W/Nb thermocouple.³⁹ Resistivity, carrier mobility, and carrier concentration measurements were carried out over the same temperature range using a custom fabricated four-point probe Hall effect system.⁴⁰ Thermal diffusivity measurements were conducted using a Netzsch LFA 457 and the specific heat capacity was measured using a Netzsch DSC 404. The thermal conductivity was calculated by $\kappa = DC_p d$, where κ is the thermal conductivity, D is the thermal diffusivity, C_p is the specific heat capacity, and d is the sample density. The measured heat capacity of $\text{Nd}_{2.84}\text{Te}_4$ was used as an estimate for all samples.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENT

The authors would like to extend special thanks to Greg Gerig and George Nakatsukasa for their aid with high temperature measurements. Additionally, we would like to thank Chi Ma at the California Institute of Technology for his assistance performing EPMA.

This work was performed at the California Institute of Technology/Jet Propulsion Laboratory under contract with the National Aeronautics and Space Administration, and was supported by the NASA Science Missions Directorate's Radioisotope Power Systems Program.

The project is based upon work supported by the National Science Foundation under grant 1102531 awarded to H. Gillman, and was also supported by the National Institute of General Medical Sciences of the National Institutes of Health under award number R25GM055052 awarded to T. Hasson. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. The work was also supported by Caltech Summer Undergraduate Research Fellowship.

REFERENCES

- (1). Bennet GL CRC Handbook of Thermoelectrics; Rowe DM., Ed.; 1995.
- (2). Schmidt G; Dudzinski L; Sutliff T Radioisotopes - Applications in Physical Sciences; Sigh N, Ed.; InTech: Reston, VA, 2011.
- (3). Fleurial JP Thermoelectric Power Generation Materials: Technology and Application Opportunities. JOM J. Miner. Met. Mater. Soc. 2009, 61 (4), 79–85.
- (4). Yang J; Caillat T Thermoelectric Materials for Space. MRS Bull. 2006, 31 (March), 224–229.
- (5). Wood C Materials for Thermoelectric Energy Conversion. Inst. Phys. 1988, 51, 459–539.
- (6). Vining CB; Fleurial JP Silicon-Germanium: An Overview of Recent Development; AIP Press, 1993; pp 87–120.
- (7). Snyder GJ; Toberer ES Complex Thermoelectric Materials. Nat. Mater. 2008, 7 (2), 105–114. [PubMed: 18219332]
- (8). May AF; Fleurial JP; Snyder GJ Thermoelectric Performance of Lanthanum Telluride Produced via Mechanical Alloying. Phys. Rev. B - Condens. Matter Mater. Phys 2008, 78 (12), 1–12.
- (9). May A; Snyder J; Fleurial JP Lanthanum Telluride: Mechanochemical Synthesis of a Refractory Thermoelectric Material. AIP Conf. Proc. 2008, 969, 672–678.
- (10). May AF; Singh DJ; Snyder GJ Influence of Band Structure on the Large Thermoelectric Performance of Lanthanum Telluride. Phys. Rev. B - Condens. Matter Mater. Phys. 2009, 79 (15), 1–4.
- (11). Vo T; von Allmen P; Huang C-K; Ma J; Bux S; Fleurial J-P Electronic and Thermoelectric Properties of Ce₃Te₄ and La₃Te₄ Computed with Density Functional Theory with On-Site Coulomb Interaction Correction. J. Appl. Phys. 2014, 116 (13), 133701.
- (12). Ma JM; Clarke SM; Zeier WG; Vo T; Von Allmen P; Snyder GJ; Kaner RB; Fleurial JP; Bux SK Mechanochemical Synthesis and High Temperature Thermoelectric Properties of Calcium-Doped Lanthanum Telluride La₃-XCaxTe₄. J. Mater. Chem. C 2015, 3 (40), 10459–10466.
- (13). Cheikh D; Hogan BE; Vo T; Von Allmen P; Lee K; Smiadok DM; Zevalkink A; Dunn BS; Fleurial JP; Bux SK Praseodymium Telluride: A High-Temperature, High-ZT Thermoelectric Material. Joule 2018, 2, 1–12.
- (14). Vickery RC; Muir HM Thermoelectric Properties of Rare Earth Chalcogenides. Adv. Energy Convers. 1961, 1 (0), 179–186.
- (15). Cutler M; Leavy JF; Fitzpatrick RL Electronic Transport in Semimetallic Cerium Sulfide. Phys. Rev. 1964, 133 (4A).
- (16). Cutler M; Leavy JF Electronic Transport in High-Resistivity Cerium Sulfide. Phys. Rev. 1964, 133 (4A).
- (17). Zhuze P; Sergeeva VM; Golikova OA Kinetic Processes in Rare-Earth Chalcogenides Having the Composition Ln₃X₄. Sov. Phys. Solid State 1970, 11, 2071.
- (18). Cutler M; Fitzpatrick RL; Leavy JF The Conduction Band of Cerium Sulfide Ce₃-XS₄. J. Phys. Chem. Solids 1963, 24(2), 319–327.
- (19). Gadzhiev G; Ismailov SM; Abdullaev KK; Khamidov MM; Omarov ZM Thermal and Electrical Properties of Gadolinium Sulfides at High Temperatures. High Temp. 2001, 39 (3), 407–412.
- (20). Taher SM; Gruber JB Thermoelectric Efficiency of Rare Earth Sesquisulfides. Mater. Res. Bull. 1981, 16 (11), 1407–1412.
- (21). Eliseev AA; Yarembash EI; Kuznetsov YG; Vigileva ES; Reshchikova AA; Anotonoa LI No Title. Inorg. Chem. 1964, 9, 876–881.
- (22). Ramsey TH; Steinfink H; Weiss EJ The Phase Equilibria and Crystal Chemistry of the Rare Earth-Group VI Systems. IV. Lanthanum-Tellurium. Inorg. Chem. 1965, 4 (8), 1154–1157.

- (23). Danielson LR; Raag V; Wood C No Title. In Intersociety Energy Conversion Engineering Conference Proceedings; 1985; p 3.531–3.535.
- (24). Golikova OA; Rudnik IM; Sergeeva VM; Kazanin MM; Tkalenko EN On the Conductivity of Rare-earth Metal Chalcogenides $\text{Ln}_{3-x}\text{X}_4$ ($0 \leq x \leq 0.33$). *Phys. Status Solidi A* 1976,37 (1) 199–203.
- (25). Ascroft NW; Mermin ND *Solid State Physics*; Harcourt College, 1976.
- (26). Okamoto H Nd-Te (Neodymium-Tellurium). In: *Alloy Phase Diagrams*, Second Ed Ed. Massalski TB, ASM Int. Mater. Park. Ohio 1990, 3, 2814–2817.
- (27). Cox WLL; Steinfink H; Bradley WFF The Structure Refinement of La_2Te_3 , a Th_3P_4 Type Structure. *Inorg. Chem.* 1966, 5 (2), 318–319.
- (28). Pei Y; Shi X; LaLonde A; Wang H; Chen L; Snyder GJ Convergence of Electronic Bands for High Performance Bulk Thermoelectrics. *Nature* 2011, 473 (7345), 66–69. [PubMed: 21544143]
- (29). Baroni, S; The PWSCF Code. <http://www.pwscf.org>.
- (30). Kohn W; Sham LJ. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* 1965, 140 (4A), A1133–A1138.
- (31). Burke K; Ernzerhof M; Perdew JP Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77 (18), 3865. [PubMed: 10062328]
- (32). Anisimov VI; Zaanen J; Andersen OK Band Theory and Mott Insulators. *Phys. Rev. B* 1991, 44, 943.
- (33). Anisimov VI; Solovyev IV; Korotin MA; Czyzyk MT; Sawatzky GA Density-Functional Theory and NiO Photoemission Spectra. *Phys. Rev. B* 1993, 48 (23), 16929–16934.
- (34). Cococcioni M; de Gironcoli S Linear Response Approach to the Calculation of the Effective Interaction Parameters in the LDA + U Method. *Phys. Rev. B* 2005, 71 (3), 035105.
- (35). Holzwarth NAW; Tackett AR; Matthews GE A Projector Augmented Wave (PAW) Code for Electronic Structure Calculations, Part I: Atompaw for Generating Atom-Centered Functions. *Comput. Phys. Commun.* 2001, 135 (3), 329–347.
- (36). Tackett AR; Holzwarth NAW; Matthews GE A Projector Augmented Wave (PAW) Code for Electronic Structure Calculations, Part II: Pwpaw for Periodic Solids in a Plane Wave Basis. *Comput. Phys. Commun.* 2001, 135 (3), 348–376.
- (37). Marzari N; Vanderbilt D; De Vita A; Payne MC Thermal Contraction and Disorder of the Al(110) Surface. 1999, 82, 3296.
- (38). Mitarov RG; Tikhonov VV; Vasil'ev LN; Oskotskij VS; Golubkov AV; Smirnov IA Specific Heat of Pr_3Te_4 and La_3Te_4 . *Phys. Status Solidi A* 1975, 30, 496–500.
- (39). Wood C; Zoltan D; Stapfer G Measurement of Seebeck Coefficient Using a Light Pulse. *Rev. Sci. Instrum.* 56 (5 pt.1), 719–722.
- (40). Borup KA; Toberer ES; Zoltan LD; Nakatsukasa G; Errico M; Fleurial JP; Iversen BB; Snyder GJ Measurement of the Electrical Resistivity and Hall Coefficient at High Temperatures. *Rev. Sci. Instrum.* 2012, 83 (12).

Figure 1. (A) Electronic density of states for $\text{Nd}_{3-x}\text{Te}_4$ and $\text{La}_{3-x}\text{Te}_4$, band structure diagrams for (B) $\text{La}_{3-x}\text{Te}_4$ and (C) $\text{Nd}_{3-x}\text{Te}_4$. (D) Predicted Seebeck coefficients as a function of carrier concentration for $\text{Nd}_{3-x}\text{Te}_4$ and $\text{La}_{3-x}\text{Te}_4$ calculated using density functional theory.

Figure 2.

(A) X-ray diffraction pattern on a ground compact of $\text{Nd}_{2.78}\text{Te}_4$ including profile fit, difference, and residuals obtained by performing Rietveld refinement. The measured pattern corresponds well with the Th_3P_4 structure type, and does not indicate the presence of any secondary phases. The two broad peaks near 22° and 26° 2θ are residual background from a Kapton film used to protect the air-sensitive samples. (B) BSE SEM image of a representative sample ($\text{Nd}_{2.84}\text{Te}_4$). The uniformity of the image contrast reflects the homogeneity of the sample. Dark areas are indicative of sample porosity.

Figure 3.

(A) X-ray diffraction patterns for pellets of $\text{Nd}_{3-x}\text{Te}_4$ at various compositions. The range of compositions Nd_3Te_4 through $\text{Nd}_{2.78}\text{Te}_4$ agree with a phase-pure cubic Th_3P_4 structure type. An oxide-contaminated pattern is given here as an example, with the largest non-overlapping oxide peak labeled. The $\text{Nd}_{2.67}\text{Te}_4$ sample adopts the orthorhombic Th_2S_3 structure type. (B) XRD pattern for $\text{Nd}_{2.67}\text{Te}_4$ before and after a 4-day anneal at 1373 K, showing the expected phase transition from the Th_2S_3 to the Th_3P_4 structure type. (C) XRD pattern for Nd_3Te_4 before and after a 7-day anneal at 1173 K, showing no phase transition. The largest non-overlapping oxide peak is labeled with an "O".

Figure 4.

(A) WDS calculated vs. Hall measured carrier concentrations for $\text{Nd}_{3-x}\text{Te}_4$ samples, showing excellent agreement between calculated and measured values. (B) Temperature-dependent resistivity for $\text{Nd}_{3-x}\text{Te}_4$ samples compared to $\text{La}_{3-x}\text{Te}_4$.¹³ $\text{Nd}_{3-x}\text{Te}_4$ showed more resistive character relative to $\text{La}_{3-x}\text{Te}_4$ at equivalent vacancy concentrations. (C) Plot of carrier mobility vs. carrier concentration at 600 K for $\text{Nd}_{3-x}\text{Te}_4$ and $\text{La}_{3-x}\text{Te}_4$, showing a wider range in $\text{Nd}_{3-x}\text{Te}_4$.¹³ The increase in mobility agrees with the decrease in carriers. SPB modeling was based on the $\text{Nd}_{2.78}\text{Te}_4$ sample with $n_H = 2.72 \times 10^{21} \text{ cm}^{-3}$ with $T = 600$

K, $m^* = 3.93 m_e$, $\mu_o = 4.45 \text{ cm}^2/\text{V-s}$, and $\kappa_L = 0.56 \text{ W/m-K}$. (D) High-temperature electron mobility for $\text{Nd}_{3-x}\text{Te}_4$ compared with $\text{La}_{3-x}\text{Te}_4$.¹³ The change in behavior near 850 K indicates the activation of a higher energy band from broadening of the Fermi-Dirac distribution.

Figure 5.

(A) Seebeck vs. temperature for $\text{Nd}_{3-x}\text{Te}_4$ compared against data for $\text{La}_{3-x}\text{Te}_4$.¹³ $\text{Nd}_{3-x}\text{Te}_4$ showed a near 20% increase in Seebeck at similar vacancy concentrations. (B) Pisarenko plot (Seebeck vs. carrier concentration) at 300 K comparing single-band (SPB) models for $\text{Nd}_{3-x}\text{Te}_4$ with different effective masses and a semi-empirical multi-band model for $\text{La}_{3-x}\text{Te}_4$ at 300 K showing similar transport at room temperature.¹³ (C) Pisarenko plot at 600 K comparing single-band (SPB) models for $\text{Nd}_{3-x}\text{Te}_4$ with different effective masses and a semi-empirical multi-band model for $\text{La}_{3-x}\text{Te}_4$ at 600 K showing a departure of $\text{Nd}_{3-x}\text{Te}_4$ from the model for $\text{La}_{3-x}\text{Te}_4$, requiring higher masses to describe the transport in

$\text{Nd}_{3-x}\text{Te}_4$.¹³ (D) Power factor (S^2/ρ) vs. temperature for various vacancy concentrations.¹³
The similar power factor of $\text{Nd}_{3-x}\text{Te}_4$ compared to $\text{La}_{3-x}\text{Te}_4$ results from the gains in the Seebeck coefficient of $\text{Nd}_{3-x}\text{Te}_4$ being offset by the increased resistivity.

Figure 6.

(A) Temperature dependent thermal conductivity of $\text{Nd}_{3-x}\text{Te}_4$ compared to that of $\text{La}_{2.74}\text{Te}_4$.¹³ (B) Lattice thermal conductivities of $\text{Nd}_{3-x}\text{Te}_4$ calculated using the Wiedemann-Franz law, compared to that of $\text{La}_{2.74}\text{Te}_4$.¹³ The similarity in κ_L of $\text{Nd}_{3-x}\text{Te}_4$ and $\text{La}_{3-x}\text{Te}_4$ indicates that differences in total thermal conductivity are from differences in the electronic contribution to κ . Higher carrier concentration $\text{Nd}_{3-x}\text{Te}_4$ samples were omitted due to strong deviations from the Wiedemann-Franz law. (C) zT vs. temperature for $\text{Nd}_{3-x}\text{Te}_4$ compared to that of $\text{La}_{2.74}\text{Te}_4$.¹³ A zT of 1.2 was achieved using $\text{Nd}_{2.78}\text{Te}_4$ at

1273 K, representing a 10% improvement over $\text{La}_{2.74}\text{Te}_4$. (D) zT as a function of carrier concentration at 600 K for $\text{Nd}_{3-x}\text{Te}_4$.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Table 1.

Theoretical and measured densities of $\text{Nd}_{3-x}\text{Te}_4$ compacts obtained via Archimedes method. Measured densities were above 96% of theoretical values calculated from nominal compositions.

Nominal Composition	Theoretical Density (g cm^{-3})	Measured Density (g cm^{-3})
Nd_3Te_4	7.46	7.17
$\text{Nd}_{2.90}\text{Te}_4$	7.34	7.27
$\text{Nd}_{2.86}\text{Te}_4$	7.30	7.24
$\text{Nd}_{2.79}\text{Te}_4$	7.23	7.22
$\text{Nd}_{2.74}\text{Te}_4$	7.16	7.12
$\text{Nd}_{2.72}\text{Te}_4$	7.14	7.08

Table 2.

Nominal compositions of the samples analyzed, listed with corresponding experimental compositions measured using wavelength dispersive spectroscopy (WDS).

Nominal Composition	WDS Composition
Nd ₃ Te ₄	Nd ₃ Te ₄
Nd _{2.90} Te ₄	Nd _{2.92} Te ₄
Nd _{2.86} Te ₄	Nd _{2.90} Te ₄
Nd _{2.79} Te ₄	Nd _{2.86} Te ₄
Nd _{2.74} Te ₄	Nd _{2.84} Te ₄
Nd _{2.72} Te ₄	Nd _{2.78} Te ₄