Thermoelectric Properties of $Nb_3Sb_xTe_{7-x}$ Compounds

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Abstract

Niobium antimony telluride, $Nb_3Sb_xTe_{7-x}$, was synthesized and tested for thermoelectric properties in the Thermoelectrics group at the Jet Propulsion Laboratory. The forty atoms per unit cell of $Nb_3Sb_2Te_5$ and its varied mixture of atoms yield a complicated structure, suggesting that $Nb_3Sb_2Te_5$ and related compounds may exhibit low thermal conductivity and hence a higher ZT value. $Nb_3Sb_xTe_{7-x}$ compounds were synthesized and subsequently analyzed for their Seebeck voltage, heat conduction, and electrical resistivity. Results indicate that $Nb_3Sb_2Te_5$ is a heavily doped semiconductor whose thermoelectric properties are compromised by compensating n-type and p-type carriers. Attempts to dope in favor of either carrier by varying the Sb:Te ratio yielded samples containing secondary metallic phases that dominated the transport properties of the resulting compounds.

Introduction

The search for more efficient thermoelectric materials has largely explored the space of binary compounds and has since moved on to investigating ternary compounds. One such ternary compound is $Nb_3Sb_2Te_5$, a material first synthesized in 1966 at the University of Oslo by Furuseth and Kjekshus.[1] Although its structure has been previously investigated in X-ray diffraction experiments, the compound has not been thoroughly tested for its thermoelectric properties.

$Nb_3Sb_2Te_5$ was first considered as a possible thermoelectric material by Jensen and Kjekshus, who predicted $Nb_3Sb_2Te_5$ to be a semiconductor based on the accounting of electrons in compounds with polyanions and polycations.[2] The constituent elements of $Nb_3Sb_2Te_5$ also made the compound an attractive target for thermoelectric studies, as antimony and tellurium are often found to be components of good thermoelectrics such as $Bi_2Sb_{0.05}Te_{2.95}$.

In addition, the complex crystal structure of $Nb_3Sb_2Te_5$ showed promise for lower thermal conductivity, and hence, higher ZT values. The $Nb_3Sb_2Te_5$ unit cell contains four $Nb_3Sb_2Te_5$ units, with each unit containing ten atoms,[1] yielding a complicated structure with forty atoms per unit cell and varied atomic composition.

In this study, the potential of $Nb_3Sb_2Te_5$ as a thermoelectric material was examined via tests on Seebeck coefficient, thermal conductivity, Hall mobility, and electrical resistivity. Doped variations of $Nb_3Sb_xTe_{7-x}$ which altered the antimony and tellurium ratios were investigated similarly for thermoelectric potential.

Experimental

Samples of $Nb_3Sb_xTe_{7-x}$ were made from powders of 99.95% (Nb_3SbTe_6, $Nb_3Sb_2Te_5$, $Nb_3Sb_3Te_4$) or 99.8% niobium (all subsequent samples), 99.999% antimony, and 99.999% tellurium. Samples were prepared in argon environments, heated to 973 K, and hot pressed 20,000 psi for two hours. Compositions tested included the parent compound $Nb_3Sb_2Te_5$, as well as the doped compounds Nb_3SbTe_6, $Nb_3Sb_3Te_4$, $Nb_3Sb_{1.5}Te_{5.5}$, $Nb_3Sb_4Te_3$, $Nb_3Sb_{2.95}Te_{4.05}$, $Nb_3Sb_{3.5}Te_{3.5}$, $Nb_3Sb_{3.05}Te_{3.95}$, $Nb_3Sb_5Te_2$, and Nb_3Sb_6Te. Average sample density was 93%.

Hot-pressed samples were measured for Seebeck coefficient, thermal conductivity, electrical resistivity, and Hall effect at room temperature. Seebeck coefficents were also monitored from room temperature to 673 K, and resistivity measurements from room temperature to 773 K

Microprobe analysis was conducted to elucidate chemical compositions of the samples using a JEOL JXA-733 electron superprobe operating at 20×10^3 volts of accelerating potential and 15×10^{-9} amps of probe current.

Table 1: Room Temperature Properties for $Nb_3Sb_xTe_{7-x}$

Sb:Te	Seebeck (μV/K)	Resistivity (mΩcm)	Hall effect (cm^2/Vs)	Th. Cond. (mW/cmK)
1:6	7	0.19	-5	20
1.5: 5.5	7	0.53	-1	28
2:5	14	2.48	-3	19
2.95:4.05	52	2.93	-5	23
3:4	22	3.71	-4	23
3.05:3.95	44	2.19	-5	19
3.5:3.5	35	1.02	-3	23
4:3	21	0.57	2	26
5:2	7	0.25	9	20
6:1	-2	0.14	9	22

Results

Results from microprobe analysis showed that only $Nb_3Sb_2Te_5$ of the compounds tested is in single phase, while all others are of nominal composition. Samples with nominal $x < 4$ showed only a small variation of 0.1, which is in the resolution limit of the microprobe, in x from $x = 2.0$. Samples with nominal $x < 2$, rich in Te, showed $NbTe_2$ as a second phase. Samples with nominal $x > 2$, rich in Sb, showed $NbSb_2$ as a second phase. Samples with nominal $x \geq 4$ showed ternary phase with $x = 2.4$ in addition to $NbSb_2$.

The samples tested share similar thermoelectric properties at room temperature (Table 1), particularly in terms of thermal conductivity, which averages at 23±5 mW/cmK. The Seebeck coefficients of the compounds were low, with the highest at 52 μV/K for $Nb_3Sb_{2.95}Te_{4.05}$ and the lowest at –2 μV/K for Nb_3Sb_6Te. Other than Nb_3Sb_6Te, all Seebeck coefficients were positive.

The electrical resistivity of the series of compounds is quite low. Compounds with 2 to 3.5 antimony atoms per $Nb_3(Sb, Te)_7$ had resistivities ranging from 1 mΩcm to nearly 4 mΩcm for $Nb_3Sb_3Te_4$, while all other compositions had resistivities below one mΩcm, with the lowest being Nb_3Sb_6Te at barely above 0.1 mΩcm.

The Hall mobility of the series is not high, as no values exceeded ±10 cm^2/Vs. Hall mobility for compositions with more tellurium (Te atoms per unit compound ≥ 3.5) have negative mobility while compositions with more antimony (Sb atoms per unit compound ≥ 4) have positive mobility. The carrier concentration of the samples range from order 10^{20} to 10^{22} (data not shown).

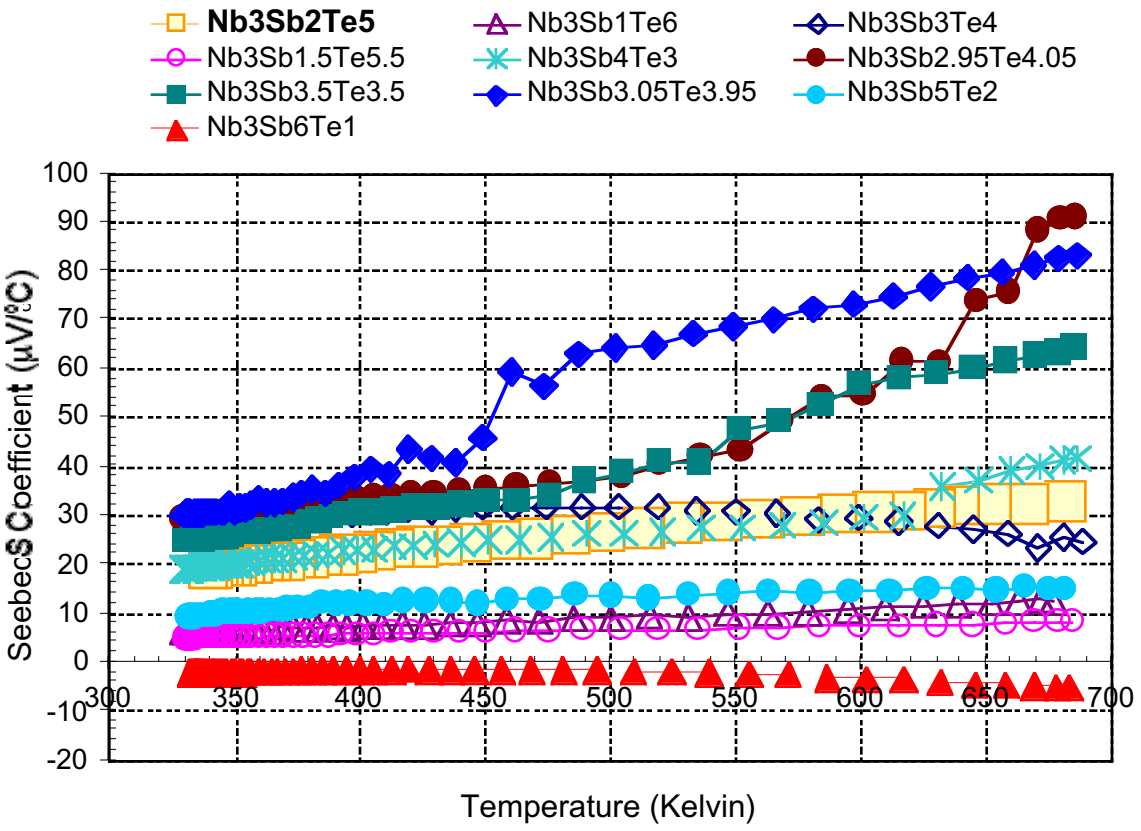

Figure 1: Seebeck Coefficients vs. Temperature Data for the $Nb_3Sb_xTe_{7-x}$ Series

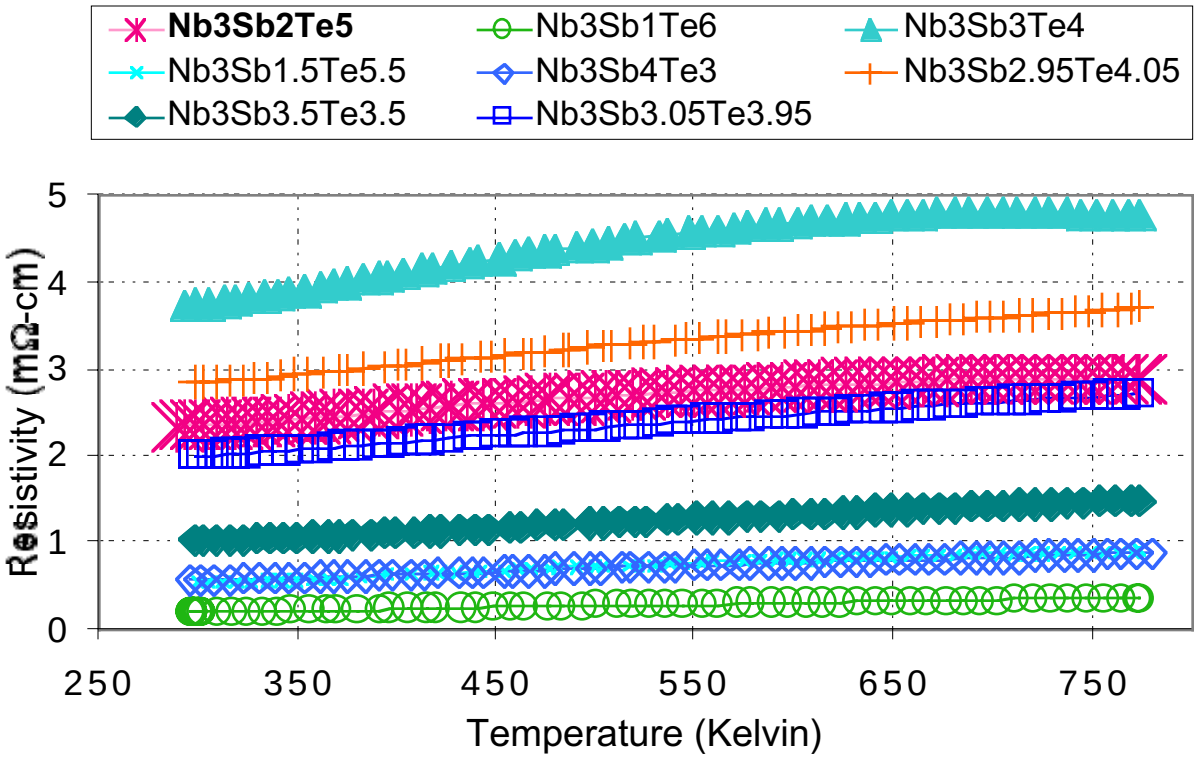

Figure 2: Resistivity vs. Temperature Data for the $Nb_3Sb_xTe_{7-x}$ Series

For high temperature measurements of Seebeck coefficient (Figure 1), the Seebeck tends to increase as temperature increases. This change is more dramatic for $Nb_3Sb_{2.95}Te_{4.05}$, $Nb_3Sb_{3.05}Te_{3.95}$, and $Nb_3Sb_{3.5}Te_{3.5}$ while others compounds tested increase by nearly constant increments. Two exceptions to this trend of increasing Seebeck with temperature are $Nb_3Sb_3Te_4$ and Nb_3Sb_6Te, whose Seebeck coefficients first increase with temperature before decreasing.

High temperature tests of Hall effect were conducted on Nb_3SbTe_6, $Nb_3Sb_2Te_5$, $Nb_3Sb_3Te_4$, $Nb_3Sb_{1.5}Te_{5.5}$, $Nb_3Sb_4Te_3$, $Nb_3Sb_{2.95}Te_{4.05}$, $Nb_3Sb_{3.5}Te_{3.5}$, and $Nb_3Sb_{3.05}Te_{3.95}$. Data indicates that resistivity climbs with temperature at a relatively constant rate in almost every case, although $Nb_3Sb_3Te_4$ levels off its resistivity near 773K (Figure 2). Mobility remained low in the high temperature tests, staying mostly within the ±5 cm^2/Vs range, with measurements other than that of $Nb_3Sb_4Te_3$ staying mostly negative. Compositions of $Nb_3Sb_3Te_4$, $Nb_3Sb_{2.95}Te_{4.05}$, and $Nb_3Sb_{3.05}Te_{3.95}$ all had Hall mobility switch signs from negative to positive, respectively near 690K, 720K, and 660K.

Discussion

$Nb_3Sb_2Te_5$ appears to be a heavily doped yet compensated semiconductor. The linear, increasing resistivity and Seebeck coefficient are typical of heavily doped semiconductors. The opposite sign of the mobility and Seebeck suggests a complex band structure near the Fermi level with compensating n-type and p-type carriers. The heavier effective mass p-type carriers dominate the Seebeck while the higher mobility n-type carriers dominate the Hall mobility and electrical conductivity.

The substitution of Sb, with less electrons than Te, for Te in $Nb_3Sb_2Te_5$ should decrease the electron concentration and increase the hole concentration. Since the electrons appear to dominate the resistivity, a rise in resistivity as x is first increased above x = 2 is expected (Figure 3). Similarly, the drop in resistivity is expected as x is decreased from x = 2.

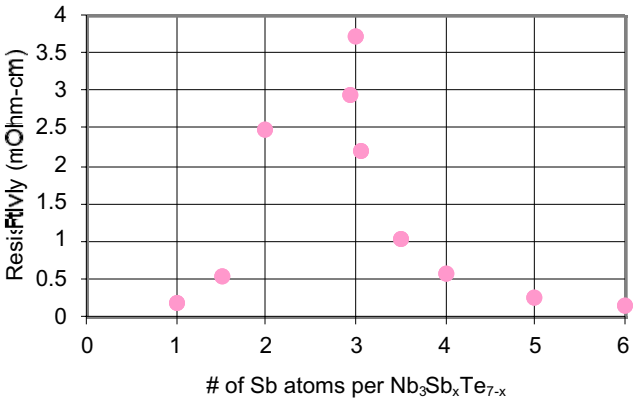

Figure 3: Room Temperature Resistivity by Composition

In a simple two carrier system, the effective Seebeck coefficient is the sum of the individual Seebeck coefficients weighted by the conductivity: $\alpha = \frac{\sigma_p \alpha_p + \sigma_n \alpha_n}{\sigma_p + \sigma_n}$ where α is the Seebeck coefficient, and σ = electrical conductivity (σ = 1/ρ, ρ is electrical resistivity)

If the individual Seebeck coefficients, α_n and α_p, ($\alpha_p > 0$, $\alpha_n < 0$) change little at these high carrier concentrations, then the change in relative conductivities of n- and p-type toward p-type by increasing x above x = 2 will also explain the modest increase in p-type Seebeck near x = 2 (Figure 4).

If further increases in p-type doping were possible, higher Seebeck coefficients might be seen by further reducing the compensation effect of the n-type carriers. However, this would occur at a cost of having a very high p-type carrier concentration which should reduce α_p.

Further increases in x, above x = 2, increase the proportion of the $NbSb_2$ in the sample. Because $NbSb_2$ is apparently a metal, it dominates the transport properties, giving samples with low Seebeck coefficients and low resistivities. Similarly, because $NbTe_2$ is apparently also a metal, samples with x < 2, also have low Seebeck coefficients and low resistivities.

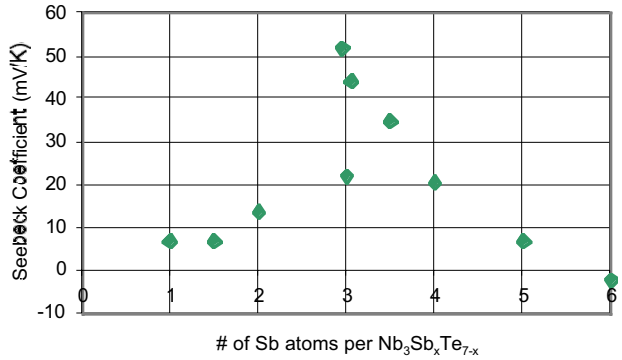

Figure 4: Room Temperature Seebeck by Composition

Conclusions

$Nb_3Sb_2Te_5$ is a heavily doped, compensated semiconductor, both of which contribute to the low Seebeck coefficient. Attempts to dope $Nb_3Sb_2Te_5$ by changing x in $Nb_3Sb_xTe_{7-x}$, produce only a small variation in x from x = 2. Such doping has a noticeable effect on the transport properties which can be explained with a simple two carrier model. However, such doping is insufficient to change the transport properties to make $Nb_3Sb_2Te_5$ a competitive thermoelectric material.

Acknowledgments

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