

Thermoelectric Properties of the Incommensurate Layered Semiconductor Ge_xNbTe_2

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Abstract

The compounds Ge_xNbTe_2 ($0.39 \leq x \leq 0.53$) have been studied for their thermoelectric properties. By changing x , the carrier concentration can be adjusted so that the material changes from a p-type metal to a p-type semiconductor. The maximum germanium concentration at about $\text{Ge}_{0.5}\text{NbTe}_2$, is also the most semiconducting composition. High and low temperature electrical resistivity, Hall effect, Seebeck coefficient, and thermal conductivity were measured. The thermal conductivity is reasonably low and glass-like with room temperature values around 20-25 mW/cm K. However, the power factor is too low to compete with state of the art materials. The maximum ZT found in these compounds is about 0.12. The low ZT can be traced to the low carrier mobility of about $10 \text{ cm}^2/\text{V s}$. The related compounds $\text{Si}_{0.5}\text{NbTe}_2$ and $\text{Ge}_{0.5}\text{TaTe}_2$ were also studied.

Keywords

thermoelectrics, thermopower, resistivity, thermal conductivity, incommensurately modulated semiconductor

Introduction

The growth of commercial applications of thermoelectric devices depends primarily on increasing the figure of merit, ZT , for thermoelectric materials. The figure of merit is

defined as $ZT = \alpha^2 \sigma T / \lambda$, where α is the Seebeck coefficient, σ the electrical conductivity, λ the thermal conductivity, and T is the absolute temperature. Materials with a large $\alpha^2 \sigma$ value, or power factor, are usually heavily doped semiconductors, such as Bi_2Te_3 . The thermal conductivity of semiconductors is usually dominated by phonon or lattice thermal conductivity. Thus, one method for finding new, advanced thermoelectric materials is to search for semiconductors with low lattice thermal conductivity.

Disordered solids such as glasses tend to have low lattice thermal conductivity due to increased phonon scattering. However in order to have a high carrier mobility a crystalline material is desired. Slack [1] has introduced the concept of an ideal thermoelectric being an electron crystal, phonon glass. With this in mind, we have studied Ge_xNbTe_2 which can have an incommensurately modulated structure and is calculated to be a low band gap semiconductor (for references see [2]).

When x in Ge_xNbTe_2 is irrational an incommensurate structure is found where ordered, crystalline layers of NbTe_2 are incommensurately modulated from one layer to the next. It has been found that the $x = 0.5$ compound is a (commensurate) semiconductor. For use as a thermoelectric x can be changed ($1/3 \leq x \leq 1/2$ are known) both to adjust the carrier concentration to the optimal level and to provide an incommensurate structure.

Experimental

Polycrystalline samples were prepared by mixing and reacting elemental powders in evacuated silica ampoules for several days at 950° C. The powders were then hot-pressed in graphite dies into dense samples, 3 mm long and 12 mm in diameter. The hot-pressing was conducted at a pressure of 1400 kg/cm² and 850° C for about 2 hours under argon atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be greater than 97% of the theoretical density.

The samples were also characterized by microprobe analysis which was performed using a JEOL JXA-733 electron superprobe operating at 20 kV and 15 nA. All samples were found to have less than 1% of impurity phases. The elemental concentrations determined from microprobe analysis are reported in table (Table 1). The experimental uncertainty is expected to be about 1% atomic. Since the crystal structure of the incommensurate structures are complex an analysis of the x-ray diffraction was not conducted at this time.

Samples in the form of disks (typically a 1.0 mm thick, 12 mm diameter slice) were cut from the cylinders using a diamond saw for electrical and thermal transport property measurements. Temperature dependence of electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity and heat capacity measurements were conducted on selected samples between 2K and 800K. A Quantum Design PPMS and indium contacts were used for resistivity measurements below room temperature. Above room temperature Hall effect measurements were performed using a custom designed vacuum furnace and pressure contacts. The 4-contact resistivity and Hall effect were measured using the method of Van der Pauw [3]. The carrier density was calculated from the Hall

coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by $n = 1/R_{\text{H}}e$, where n is the density of holes or electrons, and e is the electron charge. The Hall mobility (μ_{H}) was calculated from the Hall coefficient and the resistivity values by $\mu_{\text{H}} = R_{\text{H}}/\rho$. The uncertainty is estimated to be $\pm 0.5\%$ and $\pm 0.2 \text{ cm}^2/\text{Vs}$ for the resistivity and mobility data, respectively. The Seebeck coefficient (α) was measured with a high temperature light pulse technique [4]. The precision of the Seebeck measurement was estimated to be less than $\pm 3\%$. However, the reproducibility of the measurements when thermally cycled is less precise, this results in the larger relative error reported in Table 1. A Quantum Design PPMS was used for low temperature thermopower and resistivity measurements. Au-Fe7% vs. chromel thermocouples were used to measure both the temperatures and Seebeck voltage across the sample. The Seebeck coefficient is then referenced to copper by subtracting the Seebeck voltage of the thermocouple wires with respect to copper. Room temperature thermal conductivity was measured using the comparison method [5]. High temperature heat capacity and thermal diffusivity were measured using a flash diffusivity technique [6]. The thermal conductivity (λ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall precision in the thermal conductivity measurements was estimated to be about $\pm 10\%$.

Results and Discussion

Microprobe results in Table 1 show that there is a maximum germanium concentration attainable at $x \approx 0.5$. The excess Ge apparently phase separates; NbGe₂ was found in the microprobe analysis of the most Ge rich sample. The measured concentration of Ge is consistently less than that expected (as also found in [2]).

Table 1. Results of microprobe analysis and room temperature thermoelectric properties of the various samples tested.

Prepared x	MPA x	Car. Conc. cm^{-3}	Mobility $\text{cm}^2/\text{V s}$	Resistivity $10^{-3} \Omega \text{ cm}$	Seebeck $\mu\text{V}/\text{K}$	Th. Cond. $\text{mW}/\text{cm K}$	Lattice Th. Cond.
0.40	0.39	1 E+21	9	0.45	4	32	16
0.44	0.42	1 E+21	9	0.6	12	25	13
0.47	0.43	9 E+20	9	0.8	16	24	15
0.50	0.42	9 E+20	11	0.65	29	23	12
0.53	0.50	3 E+20	8	3	84	25	23
0.55	0.49	7 E+19	10	8.5	138	22	21
0.57	0.50	2 E+19	18	22	217	22	22
0.60	0.50	5 E+18	30	40	280	20	20
0.65	0.53	5 E+17	35	400	271	26	26
0.70	0.52	3 E+18	45	48	300	25	25
$\text{Si}_{0.5}\text{NbTe}_2$	0.50	4 E+19	7	20	98	20	19
$\text{Si}_{0.6}\text{NbTe}_2$	0.52	3 E+18	30	77	376	25	25
$\text{Ge}_{0.6}\text{TaTe}_2$	0.42	5 E+20	14	0.95	36	18	10

Resistivity

The Ge_xNbTe_2 compounds change from metals to semiconductors as x is increased (Figure 1). The above room temperature activation energy in the resistivity for the $x = 0.6$ compound is 0.12 eV which would be given by a bandgap of 0.24 eV, in agreement with band structure calculations for $\text{Si}_{0.5}\text{NbTe}_2$ [2].

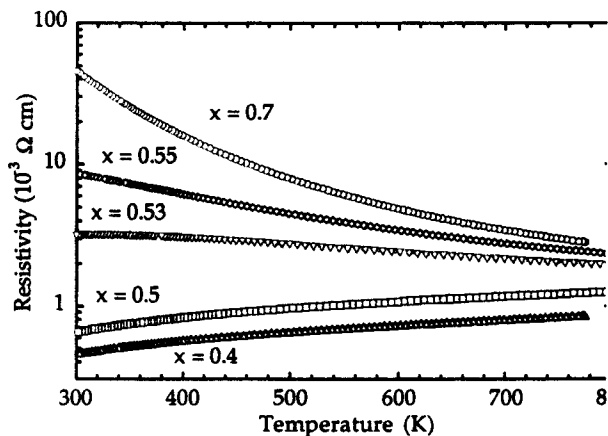


Figure 1. High temperature electrical resistivity of selected Ge_xNbTe_2 samples. Nominal not actual compositions, x , are given.

The low temperature resistivity of the semiconducting and semimetallic samples

shows signs of phase transitions. This is particularly obvious (Figure 2) in the various maxima and minima in the $x = 0.55$ resistivity. This may be due to electronic ordering (*e.g.* charge density waves) at multiple temperatures or slightly different compositions with

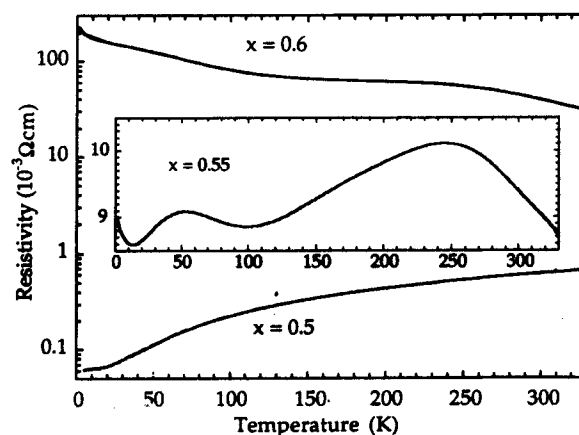


Figure 2. Low temperature electrical resistivity of some Ge_xNbTe_2 samples. Nominal not actual compositions, x , are given.

Thermopower

The Seebeck coefficient of the low resistivity samples resembles that of p-type

metals with diffusion thermopower. For an electron gas the diffusion thermopower is given by $\frac{\pi^2 k_B^2 T}{3e} \left(\frac{\partial \ln(\sigma(E))}{\partial E} \right)_{E_F}$ [7].

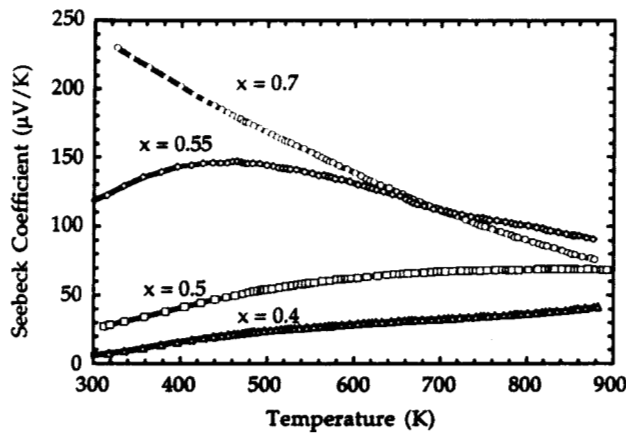


Figure 3. High temperature thermopower of selected Ge_xNbTe_2 samples. Nominal not actual compositions, x , are given.

As the Ge doping makes the samples become more semiconducting, a maximum in the thermopower appears, and migrates from high to lower temperature. Such behavior is typical of doped semiconductors.

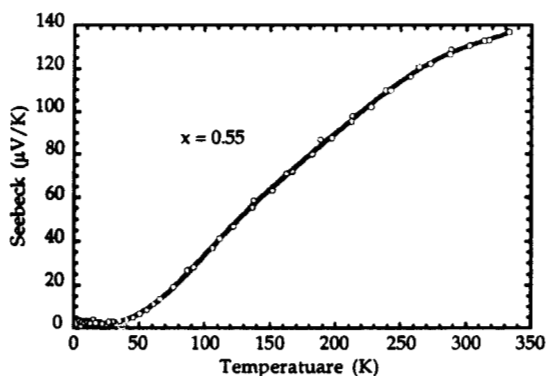


Figure 4. Low temperature thermopower of Ge_xNbTe_2 with nominal composition $x = 0.55$.

At low temperature the thermopower vanishes, as shown in (Figure 4) for $x = 0.55$.

In order to better understand the variation in the transport properties as x changes, the room temperature values for the resistivity and Seebeck coefficient are analyzed. Although the thermoelectric properties are not necessarily optimal at room temperature, this is a convenient and representative temperature.

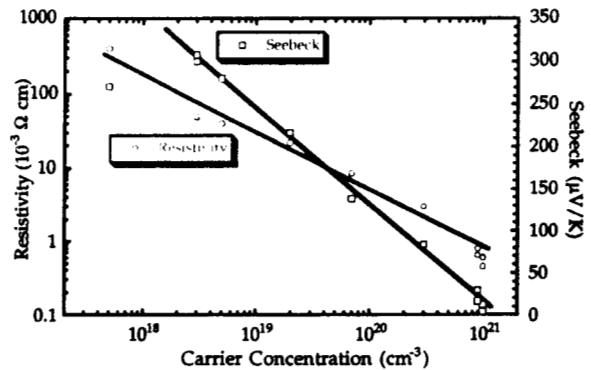


Figure 5. Room temperature thermopower and electrical resistivity of Ge_xNbTe_2 .

The transport behavior at room temperature qualitatively follows that expected from a doped semiconductor. As the carrier concentration decreases (measured by the Hall effect) the resistivity increases proportionally. The thermopower increases as the logarithm of the carrier concentration decreases. The slope of this curve (about $100 \mu\text{V}/\text{k}$ per decade) is half that expected from a simple diffusive model; suggesting the electronic structure may be changing at these carrier concentrations. Presumably, if the structure would allow, further doping by Ge would produce n-type samples.

Thermal Conductivity

The thermal conductivity λ is given by the sum of the electronic λ_E and lattice contributions λ_L . λ_E is directly related to the electronic conductivity: $\lambda_E = L\sigma T$, where L is the Lorenz factor.

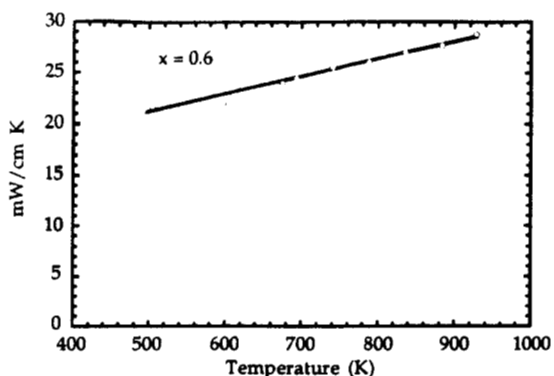


Figure 6. High temperature thermal conductivity of Ge_xNbTe_2 .

The high temperature thermal conductivity rises slightly with temperature (Figure 6) indicating multiple scattering processes. Since this sample has a low electronic conductivity, the thermal conductivity is due to the lattice contribution. Such low thermal conductivity that increases with temperature is found in complex structures such as glasses. Common crystalline materials have large lattice thermal conductivity that is proportional to $1/T$.

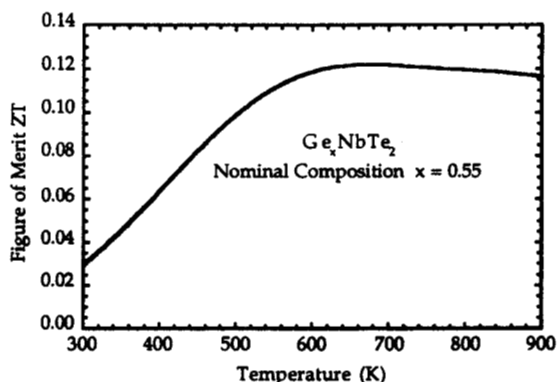


Figure 7. ZT as a function of temperature for the most promising Ge_xNbTe_2 composition.

Thermoelectric Properties

The thermal conductivity of Ge_xNbTe_2 compounds are only slightly higher than state of the art bismuth telluride alloys. However, the power factor ($S^2\sigma$) is significantly lower

than state of the art materials, leading to a maximum ZT of about 0.12 (Figure 7).

The low ZT be traced to the relatively low carrier mobility. State of the art bismuth antimony telluride alloys have a room temperature Hall mobility of 150-180 cm^2/Vs while Ge_xNbTe_2 , which has its highest power factor in a similar temperature range, has a mobility of less than 10 cm^2/Vs (for samples with reasonable carrier concentration). Low mobility μ leads to low electrical conductivity σ since $\sigma = ne\mu$, hence low power factor. Similar mobility was found in the related heavily doped compounds Si_xNbTe_2 and Ge_xTaTe_2 (Table 1), thus we find it unlikely that replacement of Ge by Si or Nb by Ta will dramatically improve the thermoelectric properties.

Summary

The compounds Ge_xNbTe_2 have been studied for their thermoelectric properties because of their complex, often incommensurately modulated, structure and promising electronic properties. By changing x , the carrier concentration can be adjusted so that the material changes from a p-type metal to a p-type semiconductor. The maximum germanium concentration that could be synthesized is at about $x = 0.5$, which is also the most semiconducting composition. Since higher Ge concentrations could not be synthesized, no n-samples were observed.

The general electronic properties of Ge_xNbTe_2 can be understood in terms of a p-type semiconductor with variable carrier concentration as determined by the Hall effect. A close inspection of the low temperature data reveals a complex array of electronic transitions which is probably related to the subtle structural changes known in these compounds.

The thermal conductivity is reasonably but not exceptionally low. However, the power

factor is too low to compete with state of the art materials. This can be traced to the relatively low carrier mobility. Replacement of Ge by Si or Nb by Ta does not increase the mobility. The maximum ZT found in these compounds is about 0.12.

Acknowledgments

We would like to thank A. Borshchevsky, A. Zoltan, L. D. Zoltan, and S. Chung for their help on this project. This work was carried out at the Jet Propulsion Laboratory-California Institute of Technology, under contract with National Aeronautics and Space Administration and supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E407.

References

- [1] G. Slack, in *Thermoelectric Handbook*, edited by M. Rowe (CRC, Boca Raton, 1995), p. 407.
- [2] J. Gareh, F. Boucher, and M. Evain, *Eur. J. Solid State Inorg. Chem.* **33**, 355 (1996).
- [3] L. J. van der Pauw, *Philips Res. Repts.* **13**, 1 (1958).
- [4] C. Wood, L. D. Zoltan, and G. Stapfer, *Rev. Sci Instrum.* **56**, 719 (1985).
- [5] D. M. Rowe, *Thermoelectric Handbook* (CRC, Boca Raton, 1995).
- [6] J. W. Vandersande, C. Wood, A. Zoltan, *et al.*, in *Thermal Conductivity* (Plenum, New York, 1988), p. 445.
- [7] R. D. Barnard, *Thermoelectricity in Metals and Alloys* (Wiley, New York, 1972).