ELECTRICAL AND THERMAL TRANSPORT IN LANTHANUM TELLURIDE

C. Vining*, C. Wood*, J. Parker*, A. Zoltan*, L. Danielson**, and M. Alexander**

*Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109
**Thermo Electron Corporation, Waltham MA 02254

ABSTRACT

High temperature electrical and thermal transport properties are reported for Th_3P_4-type $LaTe_y$ with nominal composition between y=4/3 and y=3/2. Electrical resistivity, Seebeck coefficient, Hall coefficient, Hall mobility and thermal conductivity data are presented between 300 K and 1300 K. The figure of merit is found to increase with increasing temperature and exhibits a peak of about 1 x 10^{-3}/K at 1200 K as a function of composition for y=1.46. Simple parametric relations are presented which describe the Hall factor, electrical resistivity, Seebeck coefficient, and thermal conductivity over the entire temperature and composition range studied.

INTRODUCTION

Rare earth chalcogenides with the Th_3P_4 defect structure are promising n-type thermoelectric materials for high temperature electrical power generation. Values for the figure of merit ($Z=S^2/k\rho$) from 0.42x10^{-3} [1,2] to 1.0x10^{-3} at 1300 K have been reported [3] for the lanthanum telluride system. The high figure of merit values result in part from the relatively high effective mass and Hall mobility values and relatively low thermal conductivity values [1]. Previous studies, however, have not covered the entire single phase region with systematic results. In order to determine the composition which yields the optimum figure of merit, a systematic study of all of the high temperature transport properties has been undertaken covering the entire composition range. Each transport property has been found to vary in a systematic and physically reasonable way as a function of nominal composition.

EXPERIMENTAL DETAILS

Lanthanum telluride samples were prepared by reaction of stoichiometric mixtures of high purity lanthanum and tellurium in sealed quartz ampules, followed by melting in closed tungsten crucibles. The resulting slugs were ground and vacuum hot pressed. The electrical resistivity was determined from 300 K to 1300 K using a four probe dc technique simultaneously with a differential Seebeck coefficient technique, described elsewhere [4]. Further details on sample preparation, high temperature electrical resistivity and Seebeck coefficient results are described in an accompanying paper in these proceedings [5]. The thermal conductivity was calculated from thermal diffusivity and heat capacity data determined simultaneously using a flash technique between 600 K and 1300 K [6]. Electrical resistivity and Hall coefficient measurements were performed between 300 K and 1200 K using a switched dc van der Pauw's technique [7].

RESULTS

All of the transport properties of $LaTe_y$ are strong functions of the composition, y. An accurate measure of the composition is therefore essential to an understanding of the transport properties. In this study, the value of y refers to the nominal composition as determined by the ratio of tellurium to lanthanum employed in the preparation procedure. The nominal carrier concentration (n_y) is given by

$$n_y/n_o = (12/y - 8) \qquad (1),$$

where $n_o = 4.49 \times 10^{21}$ is the carrier concentration of the fully filled structure. Since the nominal composition is difficult to control, calculated n_y values may provide an inaccurate estimate of the actual carrier concentration, particularly for low carrier concentration samples with y near 1.5. Hall coefficient (R_H) measurements provide a direct estimate of the carrier concentration (n), if

the Hall factor (r), defined by the ratio of the Hall (μ_H) and drift (μ_d) mobilities

$$r = R_H ne = \mu_H/\mu_d \qquad (2)$$

(where e=1.6 x 10^{-19} C), can be properly accounted for.

Figure 1 shows Hall coefficient measurements as a function of temperature for six samples of $LaTe_y$. The Hall coefficient is independent of temperature and systematically decreases with increasing tellurium content, y. The Hall factor, estimated from the nominal composition and measured Hall coefficient by $R_H n_y e$, is shown in Figure 2 as a function of nominal carrier concentration. The estimated Hall factor varies from 4.1 to 0.71 as the carrier concentration increases to the maximum value, n_o, similar to previous results for the Hall factor of $Ce_{3-x}S_4$ [8]. The solid line in Figure 2, given by

$$r = 0.71\ (n/n_o)^{-0.56} \qquad (3),$$

provides a relationship between the Hall coefficient and the carrier concentration. For the remainder of this paper, n refers to the carrier concentration calculated from R_H (solid lines in Fig. 1) by substituting Eq. 3 into Eq. 2 and solving for n. The experimental transport properties correlate somewhat better with n estimated in this manner than with either the composition (y) or carrier concentrations estimated from the composition (n_y).

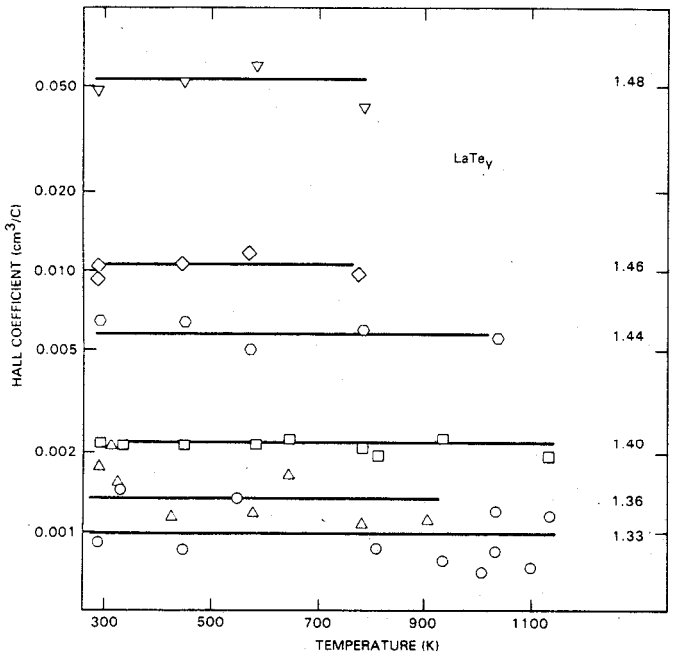

FIGURE 1: The Hall Coefficient as a function of temperature for six samples of lanthanum telluride.

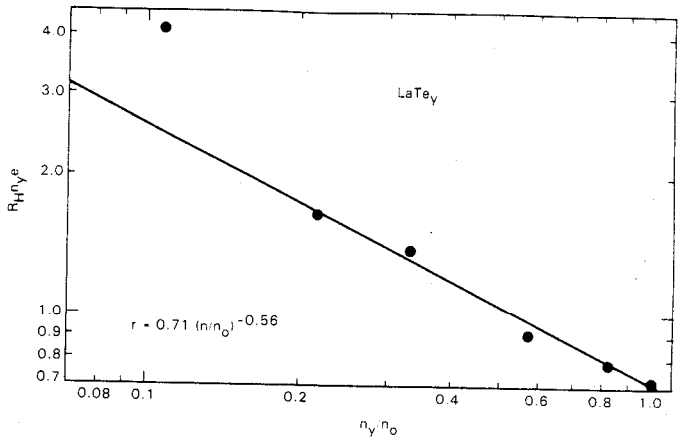

FIGURE 2: The Hall factor, $R_H n_y e$, as a function of nominal carrier concentration for six samples of lanthanum telluride.

Figures 3 and 4 show the closely related quantities Hall mobility and electrical resistivity as a function of carrier concentration. The Hall mobility decreases with increasing temperature and with increasing carrier concentration. The electrical resistivity increases with increasing temperature and decreases with increasing carrier concentration. The solid lines in Figures 3 and 4 were calculated from

$$\rho = 0.21 + 6.4 \times 10^{16}\, T^{3/2}\, r/n \qquad (4),$$

which accurately reproduces the temperature and carrier concentration dependence of the electrical resistivity.

Figure 5 shows the Seebeck coefficient divided by temperature (S/T) as a function of carrier concentration. The Seebeck coefficient is seen to vary nearly linearly with temperature and decreases with increasing carrier concentration. The temperature and carrier concentration dependence of the Seebeck coefficient is accurately described by

$$S = 0.068\ T\ n^{-2/3} \qquad (5),$$

as indicated by the solid line in Figure 5 and in good agreement with previous results on $Ce_{3-x}S_4$ [8]. Equation 5 has the form of the theoretical expression for the Seebeck coefficient in a degenerate material. Assuming acoustic phonon scattering of the electrons, an effective mass ratio of about 3 is estimated from Eq. 5, similar to the value 3.12 reported previously for $Ce_{3-x}S_4$ [8].

Equation 5 significantly overestimates the Seebeck coefficient for the lowest carrier concentration sample in this study (n/n_o=0.07, y=1.48). As discussed elsewhere in these proceedings, the temperature dependence of the Seebeck coefficient of this sample implies

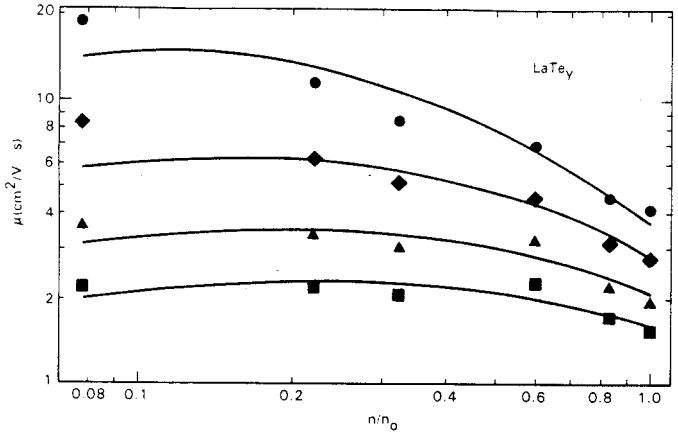

FIGURE 3: The Hall mobility as a function of carrier concentration and temperature for six samples of lanthanum telluride (circles, 300 K; diamonds, 600 K; triangles 900 K; squares, 1200 K).

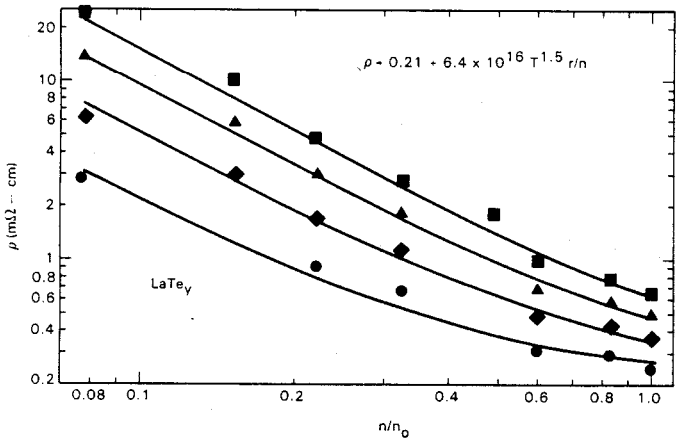

FIGURE 4: The electrical resistivity as a function of carrier concentration and temperature for eight samples of lanthanum telluride (circles, 300 K; diamonds, 600 K; triangles 900 K;squares, 1200 K).

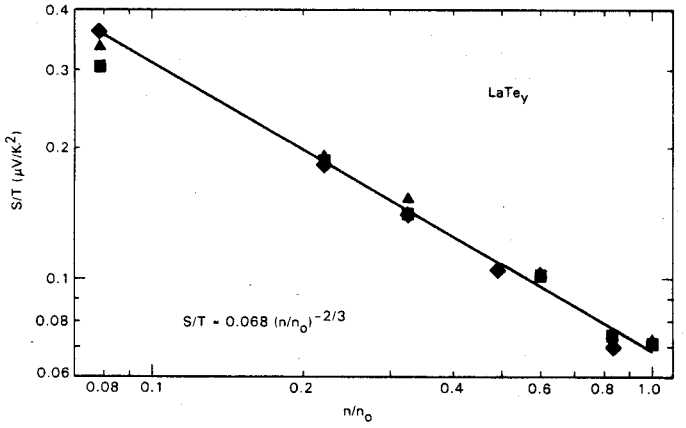

FIGURE 5: The Seebeck coefficient as a function of carrier concentration and temperature for seven samples of lanthanum telluride (circles, 300 K; diamonds, 600 K; triangles 900 K; squares, 1200 K).

the effective mass varies with temperature, even when the effect of Fermi statistics is taken into account [5]. This will be discussed below.

Figure 6 shows the electrical power factor, S^2/ρ, as a function of carrier concentration and temperature. The power factor at 1200 K reaches a maximum of about 12 mW/cm-K^2 for n/n_o=0.57 (y=1.40). The power factor for the lowest carrier concentration sample is not well reproduced by the calculated curves (based on Eqs. 3-5) due to overestimation of the Seebeck coefficient. For the higher carrier concentration samples, however, the calculated curves reproduce the experimental results reasonably well.

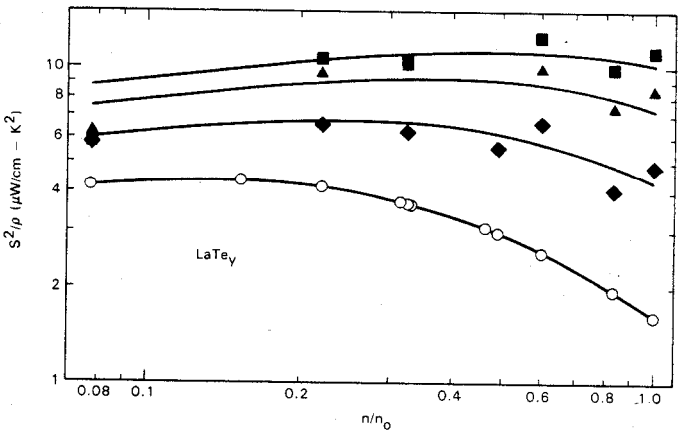

FIGURE 6: The electrical power factor as a function of carrier concentration and temperature for seven samples of lanthanum telluride (circles, 300 K; diamonds, 600 K; triangles 900 K; squares, 1200 K).

The thermal conductivity, k, is plotted as a function of the product of the electrical conductivity and temperature, σT, in Figure 7 for six samples of LaTe$_y$. The data at all temperatures fall on a single line, within experimental error, given by

$$k = 0.0066 + 2.8\,(k_B/e)^2\,\sigma T \qquad (6),$$

(k_B = 1.38 x 10^{-23} J/K). The linear relation between the thermal and electrical conductivities is consistent with a temperature and carrier concentration independent lattice thermal conductivity. The apparent Lorentz number of 2.8 is between the fully degenerate value of 3.3 and the non-degenerate, acoustic mode value of 2.0.

The figure of merit for LaTe$_y$ is shown in Figure 8 as a function of carrier concentration and temperature. The figure of merit increases with decreasing carrier concentration, reaches a maximum of about 1.0

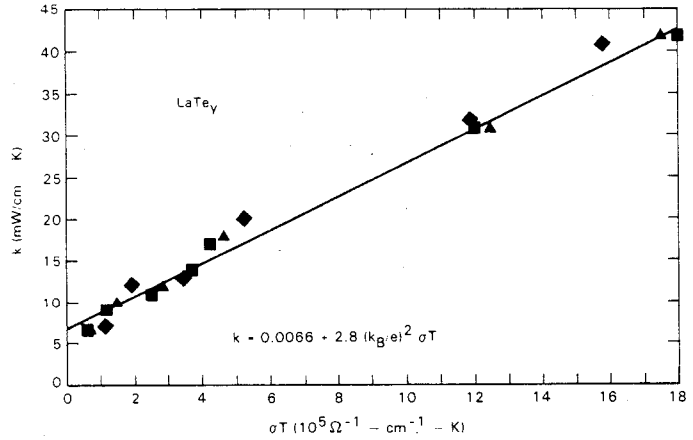

FIGURE 7: The thermal conductivity as a function of the product of the electrical conductivity and temperature for six samples of lanthanum telluride (diamonds, 600 K; triangles 900 K; squares, 1200 K).

x 10^{-3}/K (ZT=1.2) at n/n_o=0.22 for T=1200K. The lowest carrier concentration sample, n/n_o=0.07, has a slightly lower figure of merit value of about 0.9 x 10^{-3}/K, even though the electrical resistivity at this temperature is relatively large at 23 mohm-cm. However, the figure of merit calculated based upon Eqs. 3-6, is significantly higher than this value and is still increasing with decreasing carrier concentration. Since only one data point is available with a carrier concentration below the optimum value, the precise maximum figure of merit cannot be reliably estimated, but could be substantially higher than has been obtained here. Based upon the observed data in Figure 8, however, the optimum carrier concentration can be estimated as between 0.1 n_o and 0.2 n_o.

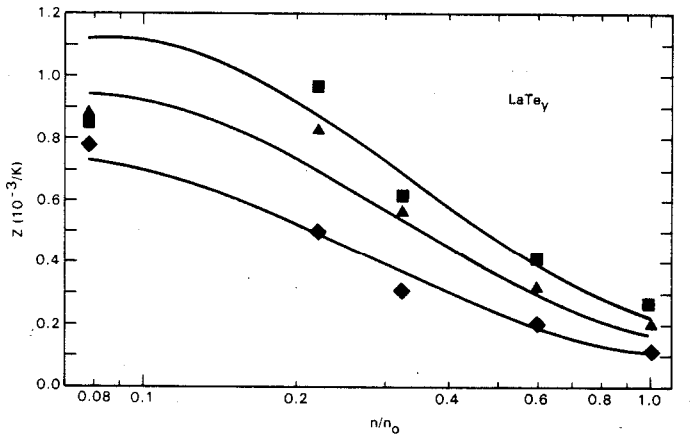

FIGURE 8: The figure of merit ZT as a function carrier concentration and temperature for five samples of lanthanum telluride (diamonds, 600 K; triangles 900 K; squares, 1200 K).

DISCUSSION

The empirical parameterizations given above for the transport properties are useful for estimation purposes, but should not be interpreted too literally. Each parameterization has a limited range of applicability and physical interpretations are somewhat conflicting. The most serious discrepancy between simple transport theory and the results on $LaTe_y$ is the variation of the Hall factor from values greater than 2 to values less than 1. Hall factor values less than 1 at the higher carrier concentrations have been attributed to non-spherical energy surfaces in $Ce_{3-x}S_4$ [8] and the same explanation probably applies to the lanthanum-tellurium system. The apparent Hall factor of 4.1 for the lowest carrier concentration sample in this study, n/n_o = 0.07 (Figure 2), must be attributed to error in the estimation of the carrier concentration from the nominal composition, since theoretically the Hall factor should not become greater than 2 under any circumstances [9]. The parameterization of the Hall factor must therefore be suspect, since Eq. 1 gives r>2 for n/n_o<0.16.

The parameterization of the electrical resistivity as the sum of a temperature and carrier concentration independent residual resistivity term and a lattice scattering term proportional to $T^{3/2}/n$, is difficult to rigorously justify. The residual resistivity term is expected to have a substantial carrier concentration dependence, which has been observed experimentally by low temperature resistivity measurements on lanthanum sulfide [10]. Further, in the degenerate regime, lattice scattering is expected to yield a linear temperature dependence, which in fact does fit the highest carrier concentration samples somewhat better than the $T^{3/2}$ term used in Eq. 4 [5]. At low carrier concentrations and high temperatures, however, the lattice scattering term dominates the resistivity, so any concentration dependence to the residual resistivity may make only a small contribution to the total resistivity. In spite of these objections, Eq. 4 is useful because the simple functional dependence on temperature and carrier concentration come remarkably close to the observed data and strongly suggest lattice scattering as the primary electron scattering mechanism.

The temperature and carrier concentration dependence of the Seebeck coefficient for a degenerate electron gas is of the same form as Eq. 5. As the carrier concentration is reduced the system eventually becomes non-degenerate and deviations from Eq. 5 should be and are observed. Elsewhere in these

proceedings the full effect of Fermi statistics has been applied to analysis of the Seebeck coefficient, assuming acoustic phonon scattering [5]. That analysis indicates the "average" effective mass must vary with temperature in order to account for the observed Seebeck coefficient for the lowest carrier concentration sample studied (n/n_o=0.07, y=1.48). Alternatively, the observed deviation from Eq. 5 may be a result of non-spherical energy surfaces and/or the influence of additional scattering mechanisms (ionized impurity, alloy disorder, etc.). These effects, however, are difficult to distinguish without additional data for samples in the lower carrier concentration region (n/n_o<0.2).

The simple relationship between the thermal conductivity and the electrical conductivity should also be examined more closely. The lattice thermal conductivity is expected to have some temperature and carrier concentration dependence, which is neglected in Eq. 6. Alloy disorder scattering and electron-phonon scattering are both expected to significantly influence the lattice thermal conductivity. Since disorder is greatest when the carrier concentration is zero in these materials, the two effects might compensate to some extent, resulting in a nearly concentration independent lattice thermal conductivity. Alternatively, the expected variation in the Lorentz number from 2 $(k_B/e)^2$ to 3.3 $(k_B/e)^2$ with increasing carrier concentration may compensate for changes in the lattice thermal conductivity with carrier concentration. In either case the linear relation shown in Figure 7 would be something of a coincidence.

Since the maximum in the figure of merit occurs in the low carrier concentration region, where the simple expressions for the transport properties provided above are least reliable (particularly for the Seebeck and Hall coefficients) a more sophisticated model will be required for reliable calculation of the figure of merit. The unusual behavior of the Hall coefficient in this system is actually an advantage, since these data provide an important constraint on the possible models. Additional data in the low carrier concentration region would also be useful in this respect. A full theoretical description of the electrical properties of $LaTe_y$ is a formidable task, however, and will require accounting for Fermi statistics, multiple electron scattering mechanisms, non-spherical energy surfaces and perhaps other factors not yet identified. Also, the lattice thermal conductivity can only be accurately estimated by using a model of the electrical properties to calculate the electrical contribution to the thermal conductivity. However, these simple parametric equations employed to fit the data are useful, in lieu of a more accurate model, in order to help pinpoint the maximum figure of merit and the concentration at which it occurs.

CONCLUSIONS

The high temperature transport properties of lanthanum telluride in the Th_3P_4 crystal structure are well described by simple, physically interpretable expressions over the temperature range 300 K to 1300 K and the composition range from $LaTe_{1.33}$ to $LaTe_{1.48}$. The highest observed figure of merit in this study is 1.0 x 10-3 /K. The maximum possible figure of merit is expected to be somewhat higher than this value and occur for a carrier concentration between n/n_o=0.1 and n/n_o=0.2.

ACNOWLEDGEMENTS

The work described in this paper was carried out at the Jet Propulsion Laboratory/ California Institute of Technology, under Contract with the National Aeronautics and Space Administration.

REFERENCES

1. V. P. Zhuze, V. M. Sergeeva and O. A. Golikova, Sov. Phys. Solid State, 11 2071 (1970); 13 6689 (1971).
2. O. A. Golikova and I. M. Rudnik, Izv. Akad. Nauk, SSSR Neorg. Mater. 14 17 (1978).
3. L. R. Danielson, V. Ragg and C. Wood, Proc. 20th Intersoc. Energy Conv. Conf. Miami Beach, FL., Aug. 18-23 (1985) (Soc. Auto. Engrs.) 3531.
4. L. Danielson, S. Matsuda, and V. Raag, Proc. 19th Intersociety Energy Conversion Engineering Conference, San Fransisco, CA. (1984).
5. L. R. Danielson, M. N. Alexander, C. Vining, R. A. Lockwood, and C. Wood, Seventh International Conference on Thermoelectric Energy Conversion, Arlington, TX, March 16-18 (1988).
6. C. Wood and A. Zoltan, Rev. Sci. Instrum 55, 235 (1984).
7. C. Wood, A. Lockwood, A. Chmielewski, J. Parker, A. Zoltan, Rev. Sci. Instrum., 55, 1 (1984).
8. M. Cutler, R. L. Fitzpatrick and J. F. Leavy, J. Phys. Chem. Solids, 24, 319 (1963).
9. J. D. Wiley, Semiconductors and Semimetals, Vol. 10, Edited by R. K. Willardson and A. C. Beer (Academic Press, New York), p. 91(1975).
10. K. Ikeda, K. A. Gschneidner, Jr., B. J. Beaudry, and T. Ito, Phys. Rev. B25 4618 (1982).