

## Some Properties of $\text{Re}_2\text{Te}_5$ -based Materials

T. Caillat\*, S. Chung, J. -P. Fleurial, G. J. Snyder, and A. Borshchevsky  
 Jet Propulsion Laboratory/California Institute of Technology  
 4800, Oak Grove Drive, MS 277-207, Pasadena, CA 91109  
 \*thierry.caillat@jpl.nasa.gov

### Abstract

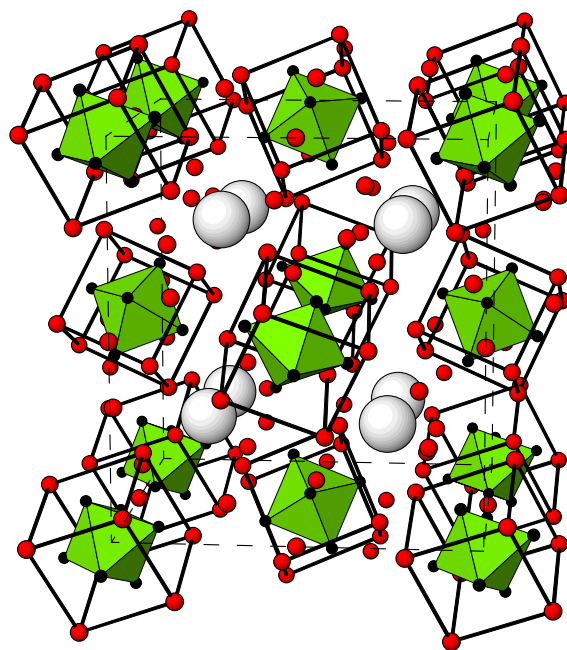
$\text{Re}_2\text{Te}_5$  is a semiconducting compound with an energy band gap of about 0.8 eV. It has a relatively complex crystal structure with 84 atoms per unit cell. Initial results obtained on p-type polycrystalline samples showed that they possess large Seebeck coefficient values but large electrical resistivity values. They also exhibit very low thermal conductivity with a room temperature value of 13 mW/cmK. Another attracting feature of  $\text{Re}_2\text{Te}_5$  is the possibility to insert a variety of atoms in the large voids (2.8 Å in diameter) of the crystal structure to form  $\text{Re}_6\text{M}_2\text{Te}_{15}$  filled compositions. The void fillers could act as phonon scattering centers, further reducing the thermal conductivity in these materials. As part of an effort to evaluate the potential of  $\text{Re}_2\text{Te}_5$ -based materials for thermoelectric applications, we are currently exploring the synthesis and properties of filled compositions as well as n-type  $\text{Re}_2\text{Te}_5$  samples. We present and discuss in this paper initial results obtained on Fe and Ag doped  $\text{Re}_2\text{Te}_5$  samples.

### Introduction

One of the new approaches for developing thermoelectric materials with superior figures of merit is to look at materials which can be referred to as “rattling” semiconductors. Originally proposed by Slack [1], the idea is that, in crystals containing loosely bound atoms, phonons should be scattered more strongly than electrons (holes). Such materials should, therefore possess both a low thermal conductivity and good electrical properties (high carrier mobility). Low lattice thermal conductivity have been measured for compounds from at least two classes of “rattling” materials: skutterudites and Chevrel compounds [2-6].

Another compound with a crystal structure that can host “rattling” atoms is  $\text{Re}_6\text{Te}_{15}$ . The crystal structure of the cluster compound  $\text{Re}_6\text{Te}_{15}$  was studied in details by Klaiber et al. [7]. This compound, with 84 atoms per unit cell, belongs to the space group  $Pbca$  with  $a=13.003\text{Å}$ ,  $b=12.935\text{Å}$  and  $c=14.212\text{Å}$ . The crystal structure presents some similarities with the Chevrel phases and the Re atoms are also arranged in octahedral  $[\text{Re}_6]$  clusters (see Figure 1). A number of voids are present in the structure and are illustrated on Figure 1. The large spheres represent the atoms that can possibly be inserted in these voids. The radius of the voids is 2.754Å [7] and therefore each of the voids is large enough to accommodate a great number of different type of atoms. Filled compositions can be represented by the formula  $\text{Re}_6\text{M}_2\text{Te}_{15}$ . Information about the thermoelectric properties of  $\text{Re}_6\text{Te}_{15}$  is rather sketchy in the literature and we have started to synthesize and measure the properties of  $\text{Re}_6\text{Te}_{15}$ -based materials. Initial results, reported in an earlier publication [7], show that, as expected from the heavy masses of the elements forming the compound as well as the large number of atoms per unit cell,

the thermal conductivity values for  $\text{Re}_6\text{Te}_{15}$  are low (~13 mW/cmK at 300K). Undoped samples are p-type and possess high Seebeck coefficient and electrical resistivity. The lattice thermal conductivity is reduced further by point defect scattering in  $\text{Re}_6\text{Te}_{15-x}\text{Se}_x$  solid solutions [6]. In addition, it was found that several filled compositions  $\text{Re}_6\text{Ag}_x\text{Te}_{15}$  with  $0.5 \leq x \leq 1.14$  could be formed. In an effort to further characterize the properties of  $\text{Re}_6\text{Te}_{15}$ -based materials, we have synthesized Fe and Ag doped samples and measured some of their properties. The results are reported and discussed in this paper.



**Figure 1:** Illustration of the  $\text{Re}_6\text{Te}_{15}$  unit cell showing the  $[\text{Re}_6]$  cluster surrounded by eight Te atoms. Large spheres representing atoms are inserted in the voids presented in the structure. Some Te atoms were omitted for clarity.

### Experimental

Single phase, polycrystalline samples of Ag and Fe doped  $\text{Re}_6\text{Te}_{15}$  were prepared by mixing and reacting elemental powders of rhenium (99.997%), tellurium (99.999%) and iron (99.999%) or silver (99.99%). The nominal compositions were  $\text{Re}_{5.5}\text{Fe}_{0.5}\text{Te}_{15}$  and  $\text{Re}_6\text{Te}_{14.5}\text{Ag}_{0.5}$ . The powders were first mixed in a plastic vial using a mixer before being loaded into a quartz ampoule which was evacuated and sealed. The ampoules were then heated at 973K for 10 days with one intermediate crushing. The samples were analyzed by x-ray diffractometry (XRD) to check that they were single phase. The powders were then hot-pressed in graphite dies into dense samples, 10 mm long and 12 mm in diameter. The hot-

pressing was conducted at a pressure of about 20,000 psi and at a temperature of 973 K 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 about 97% of the theoretical density.

The samples were also characterized by microprobe analysis (MPA) which was performed using a JEOL JXA-733 electron superprobe operating at  $20 \times 10^3$  Volts (V) of accelerating potential and  $25 \times 10^{-9}$  Amperes (A) of probe current. All samples were found to contain less than 1% of secondary phase by microprobe analysis.

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 (perpendicular to the pressing direction) for electrical and thermal transport property measurements. All samples were characterized at room temperature by Seebeck coefficient, Hall effect and electrical resistivity measurements. High temperature resistivity, Hall effect, Seebeck coefficient, thermal diffusivity, and heat capacity measurements were also conducted on selected samples between room temperature up to about 800K. The electrical resistivity ( $\rho$ ) was measured using the van der Paw technique with a current of 100 mA using a special high temperature apparatus [8]. The Hall coefficient ( $R_H$ ) was measured in the same apparatus with a constant magnetic field value of  $\sim 10,400$  Gauss. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by  $p/n = 1/R_H e$ , where  $p$  and  $n$  are the densities of holes and electrons, respectively, and  $e$  is the electron charge. The Hall mobility ( $\mu_H$ ) was calculated from the Hall coefficient and the resistivity values by  $\mu_H = R_H/\rho$ . Errors were estimated to be  $\pm 0.5\%$  and  $\pm 2\%$  for the resistivity and Hall coefficient data, respectively. The Seebeck coefficient ( $\alpha$ ) of the samples was measured on the same samples used for electrical resistivity and Hall coefficient measurements using a high temperature light pulse technique [9]. The error of the Seebeck coefficient measurement was estimated to be less than  $\pm 3\%$ . The heat capacity and thermal diffusivity were measured using a flash diffusivity technique [10]. The thermal conductivity ( $\lambda$ ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity measurements was estimated to be about  $\pm 10\%$ .

## Results and discussion

After synthesis, the compositions of the Fe and Ag doped samples were found to be  $Re_{5.56}Fe_{0.44}Te_{15}$  and  $Re_6Te_{14.6}Ag_{0.4}$ , respectively. It seems therefore that Fe atoms substitute for Re while Ag atoms substitute for Te. The room temperature properties of these samples are reported in Table I together with undoped  $Re_6Te_{15}$  and the  $Re_6Te_{12.75}Se_{2.25}$  solid solution [6].  $Re_6Te_{15}$  and the  $Re_6Te_{12.75}Se_{2.25}$  sample are p-type whereas Ag and Fe doped samples are n-type. The room temperature properties of all samples are radically different. The hole mobility is low for p -type materials whereas reasonably high electron mobility are obtained for n-type materials. The electron mobility of the Ag-doped sample is  $209 \text{ cm}^2/\text{Vs}$  at a carrier concentration of  $1.13 \times 10^{17} \text{ cm}^{-3}$ . This is comparable to values obtained for n-type  $CoSb_3$  [11] but the thermal conductivity is roughly 10 times lower for the Ag doped  $Re_6Te_{15}$  doped sample. Considering the high electrical

resistivity of the samples, the electronic component of the total thermal conductivity is negligible and, if one neglects the ambipolar contribution, the values shown in Table I can be considered as being the contribution of the lattice only. The lattice thermal conductivity is very low for all samples with a room temperature of  $13 \text{ mW/cmK}$  for  $Re_6Te_{15}$ . The lattice thermal conductivity is reduced for the ternary samples but is substantially lower for the Ag and Fe doped samples than for the Se doped. This result is somewhat surprising considering that the Se concentration is much larger than the Fe and Ag concentration in the samples. One possible explanation is that a fraction of the Fe and Ag atoms is actually being inserted inside the large voids within the Crystal structure, being efficient phonon scattering centers. Microprobe analysis obviously does not allow to distinguish whether the Fe or Ag atoms are going into substitution or onto insertion. Detailed x-ray analysis should be performed to determine the position of the doping atoms.

Table I. Some properties at room temperature for  $Re_6Te_{15}$  (1),  $Re_6Te_{12.75}Se_{2.25}$  (2),  $Re_{5.56}Fe_{0.44}Te_{15}$  (3) and  $Re_6Te_{14.6}Ag_{0.4}$  (4)

Property	1	2	3	4
Seebeck coefficient ( $\mu\text{V/K}$ )	+500	+110	-120	-10
Electrical resistivity ( $\text{m}\Omega\text{cm}$ )	8100	200	74	264
Hall mobility ( $\text{cm}^2/\text{Vs}$ )	3	13	6	209
Hall carrier concentration ( $\times 10^{17} \text{cm}^{-3}$ )	20	22	126	1.13
Thermal conductivity ( $\text{mW/cmK}$ )	13	10	5.5	7.71

The variations of the electrical resistivity, Hall mobility, and Seebeck coefficient values are reported as a function of temperature in Figures 2, 3, and 4, respectively. With the exception of the Se-doped sample, the electrical resistivity increases with increasing temperature suggesting that both electrons and holes significantly participate in the electrical conduction. For the Fe doped sample, the electrical resistivity reaches a minimum value of about  $10 \text{ m}\Omega\text{cm}$  at 700K while the Seebeck coefficient values are nearly temperature independent. The carrier mobility also decreases with increasing temperature. The power factor values ( $\alpha^2/\rho$ ) are relatively low but might be improved for samples with higher doping level. Efforts are currently in progress to prepare and characterize samples with higher electron concentrations (for example by double doping Fe-Ni or Fe-Co). For the Ag doped sample, the relatively large value for the electrical resistivity and the small Seebeck value also indicate mixed electron and hole conduction. As we mentioned before, the Hall mobility are however relatively large and indicate that electrical resistivity values comparable to state-of-the-art thermoelectric materials might be achieved for extrinsic samples with a doping level in the  $10^{19} - 10^{20} \text{ cm}^{-3}$  range. More Ag doped samples are being prepared to determine the Ag solubility limit in  $Re_6Te_{15}$  and study the impact of different Ag concentrations on the carrier concentration of the samples. Initial results indicate that much higher carrier mobility can be achieved for n-type -based materials, resulting in substantially

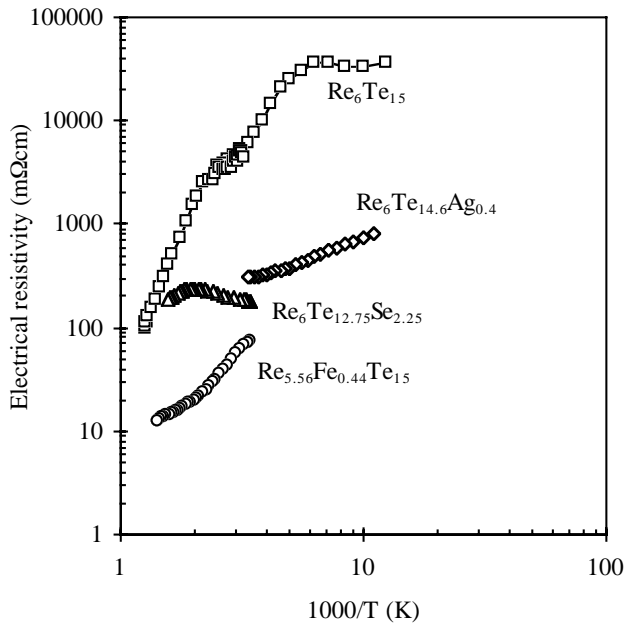


Figure 2: Electrical resistivity versus inverse temperature for some  $\text{Re}_6\text{Te}_{15}$ -based materials

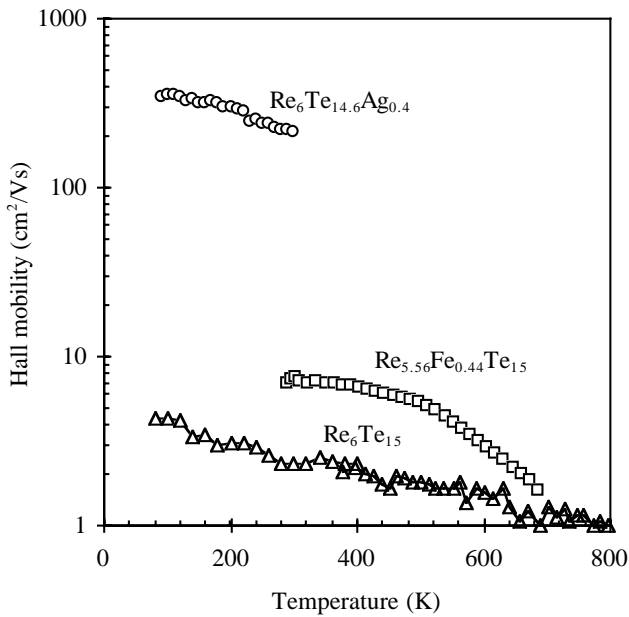


Figure 3: Hall mobility versus temperature for some  $\text{Re}_6\text{Te}_{15}$ -based materials

lower electrical resistivity values at a comparable carrier concentration.

The results of the thermal conductivity measurements are shown in Figure 5. The thermal conductivity values are compared to  $\text{Bi}_2\text{Te}_3$ -based alloys, state-of-the-art thermoelectric materials at room temperature. At room temperature, the thermal conductivity for  $\text{Re}_6\text{Te}_{15}$  is about 13 mW/cmK and is comparable to p-type  $\text{Bi}_2\text{Te}_3$ -based alloys. The thermal conductivity of  $\text{Re}_6\text{Te}_{15}$  decreases with increasing temperature following reasonably well a  $1/T$  dependence, as

expected for phonon-phonon umklapp scattering. A minimum of 7 mW/cmK is reached at 800K, significantly lower than the values obtained for state-of-the-art thermoelectric materials. For the  $\text{Re}_6\text{Se}_{2.25}\text{Te}_{12.75}$  solid solution, the thermal conductivity decreases with increasing temperature approximately as  $T^{-1/2}$ . This temperature dependence is typical of a phonon scattering by point defects. The values for the solid solution are lower than for the binary compound because of the mass and volume fluctuations introduced by the substitution of Se atoms for Te atoms. At room temperature the thermal conductivity is 10 mW/cmK, decreasing to a minimum of 6 mW/cmK at 600K. For the Fe-doped sample, the thermal conductivity values are nearly temperature independent with a value of 5.5 mW/cmK. This suggests that, in addition to point defects, other scattering mechanisms are present. As we mentioned before, it is possible that a fraction of the Fe atoms are in fact inserted in the voids, are able to move freely inside these large cavities and therefore scatter efficiently the phonons.

The minimum calculated lattice thermal conductivity for  $\text{Re}_6\text{Te}_{15}$  is 2.3 mW/cmK at room temperature [6]. At room temperature, the measured value for the Fe-doped sample is 5.5 mW/cmK, almost 3 times lower than the values obtained for  $\text{Bi}_2\text{Te}_3$ -based alloys and close to the calculated theoretical minimum. This remarkably low value suggests that figures of merit comparable at least comparable to state-of-the-art thermoelectric materials could be achieved providing the electrical properties can be optimized. Future studies are necessary to fully assess the potential of n-type  $\text{Re}_6\text{Te}_{15}$ -based materials as well as filled materials.

Figure 4: Seebeck coefficient versus temperature for some  $\text{Re}_6\text{Te}_{15}$ -based materials

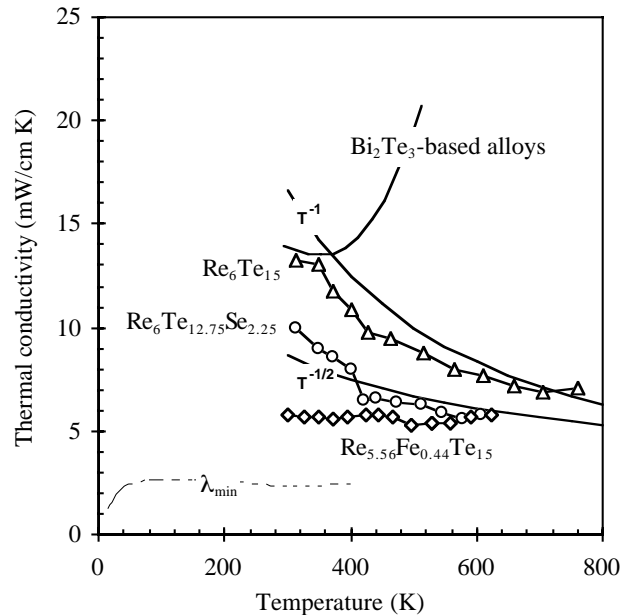


Figure 5: Thermal conductivity versus temperature for some  $\text{Re}_6\text{Te}_{15}$ -based materials. The calculated minimum lattice

thermal conductivity is also reported (see reference [6] for details of calculations). The values for p-type state-of-the-art Bi<sub>2</sub>Te<sub>3</sub> thermoelectric materials are also reported for comparison.

### Conclusion

N-type Re<sub>6</sub>Te<sub>15</sub> samples were prepared by doping with Fe and Ag. The samples are characterized by carrier mobility substantially larger than p-type materials. They are also characterized by very low thermal conductivity, significantly lower than those obtained for Bi<sub>2</sub>Te<sub>3</sub>-based alloys. The thermal conductivity is nearly temperature independent which suggests that a fraction of the doping atoms are inserted inside the large voids in the crystal structure, acting as efficient phonon scattering centers. These very low thermal conductive values combined with the reasonably large electron mobility values indicate the good potential of these materials for thermoelectric materials. Further studies are however needed to determine if the electrical properties can be further optimized and the doping level controlled. In addition, attention should be paid to study void filling as a way to control the thermal and electrical properties of these materials.

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