THERMOELECTRIC MATERIALS FOR POWER GENERATION AND REFRIGERATION --- LOW THERMAL CONDUCTIVITY IN REDUCED TiO$_2$

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INTRODUCTION

Research activities in our groups focus on the investigation of a number of novel materials that have potential to exhibit superior thermoelectric properties for energy conversion applications. Such applications include electrical power generation from waste heat, geothermal energy and solar energy, which is becoming increasingly urgent as the world energy consumption has dramatically increased over the past decades. The growing consumption of fossil energy has produced more CO_2 in the atmosphere with obvious consequences due to the greenhouse effect. Solar, wind, geothermal and even nuclear energy are clean alternatives to fossil fuels.

The figure of merit of thermoelectric materials *ZT* is basically determined by its Seebeck coefficient, electrical conductivity, and thermal conductivity. Whereas it increases with the increase of the first two parameters, it is inversely proportional to the thermal conductivity. Therefore good thermoelectric materials are often found in doped semiconductors which are midway between metals and insulators. Most of the research effort for the last thirty years or so has been trying to optimize the properties of Bi_2Te_3 based alloys in order to improve their thermoelectric capabilities, and there are recent breakthroughs in the investigation of nanostructured Bi_2Te_3, for example, see [1].

The thermoelectric properties of rutile TiO$_2$ were studied in 1950's and 1960's [2,3]. It was found that the Seebeck coefficient of rutile is negative, suggesting *n*-type carriers, and can be very large at low temperature due to phonon-drag effect. Its magnitude decreases and saturates between 500-1000 μV/K near room temperature. The thermal conductivity of bulk rutile falls in the range of 5-10 W/Km at room temperature. Introducing oxygen vacancies decreases both the thermal conductivity and Seebeck coefficient in TiO$_{2-\delta}$ [3,4]. At the same time the electrical resistivity decreases drastically due to the increase in the carrier concentration in the reduced samples.

RESULTS AND DISCUSSION

We have investigated a series of single crystal rutile TiO$_2$ samples that were annealed in hydrogen at different temperatures ranging from 750 to 1170 ^{o}C [5]. The thermal conductivity decreases with the annealing temperature, thus, with the amount of oxygen vacancies. At the same time, the Seebeck coefficient decreases as well. Figure 1 shows the temperature dependence of the thermal conductivity κ, Seebeck coefficient S and electrical resistivity ρ of the sample annealed in hydrogen at 1100 ^{o}C. The measurements were done with heat and electrical current flow perpendicular to the (101) plane of the tetragonal lattice of the rutile. The room temperature values for κ, S and ρ are 2.5 W/mK, -97 μV/K and 0.03 Ω.cm, respectively. The *ZT* of the single crystal samples is as high as 0.0085 at 393 K and shows tendency to continue to increase with the further increase of temperature. High temperature thermoelectric properties of the samples are currently being investigated. Limited reduction in S, and much
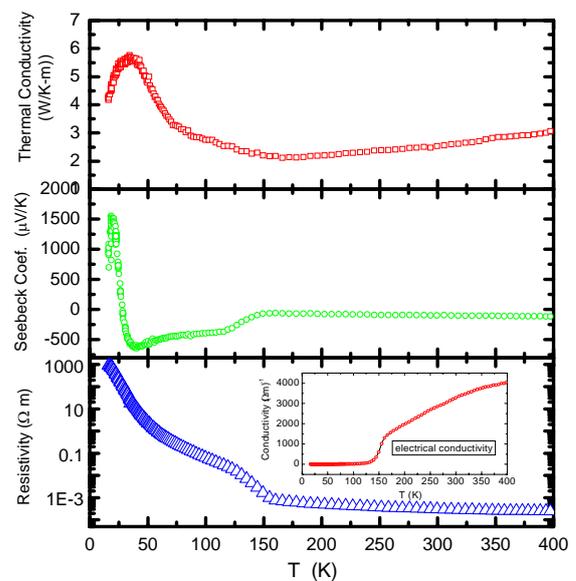

Figure 1. Thermal conductivity, Seebeck coefficient and electrical resistivityof a single crystal reduced rutileTiO$_{2-\delta}$.

reduced κ and ρ of the reduced rutile contribute to the overall improved performance of the *ZT*. The decrease in the thermal conductivity is due to defect scattering of the phonons [3].

What is also interesting is that we have observed a colossal Seebeck coefficient in these samples at low temperature. The Seebeck coefficient changes sign from negative at high temperatures to positive below ~30 K (see Figure 1), which suggests the change of majority carriers from electrons to holes. The Seebeck coefficient becomes very large at lower temperatures. The peak value varies from ~1000 μV/K for the heavily reduced sample (annealed at 1170 ^{o}C) to 60,000 μV/K for the lightly reduced sample (annealed at 780 ^{o}C). The origin of this colossal positive S is likely due to phonon drag effect [3]. On the other hand, it is possible the colossal Seebeck effect be exploited for thermoelectric device application. The power factor for the lightly reduced sample reaches 130 μW/K^{2}cm, which is 4-5 times higher than Bi$_2$Te$_3$-based materials. In addition to potential low temperature applications, understanding its origin may help us to tune and design materials that have desirable features at higher temperatures.

When we purposely induce the defect planes in the single crystal samples, we found that the thermal conductivity κ gradually decreases with the degree of reduction, *i.e.*, with the increased amount of oxygen vacancies and defect planes. It is as low as 0.83 W/Km for the heavily reduced sample at 390 K due to phonon scattering by the defects. At low temperatures κ follows a $T^{1.77}$ temperature dependence for the heavily reduced sample, which is closer to a T^2 dependence than a T^3. Such a temperature dependence indicates that the dominant phonon scattering mechanism in the sample is by dislocations rather than by defect planes, as the former is expected to exhibit T^2 dependence and the latter T^3 dependence. Further reduction of the samples may lead to more prominent role of phonon scattering by the defect planes. On the other hand, our study on the orientation dependence of the thermal transport has already shown significant role of the defect planes.

Figure 2 shows the thermal conductivity of a reduced rutile single crystal as a function of temperature. κ was measured in two directions: *a*) mainly along the (101) planes and *b*) across the (101) planes at right angle. The (101) planes are known to be the defect planes in this material. κ along the (101) planes is much higher than that across the (101) planes over the temperature range shown, suggesting large phonon scattering by the (101) planes. At the lowest temperature of the measurement, the ratio of the two is 2.4. This difference is retained at high temperatures although at a smaller percentage value. At room temperature it is about 30%. This demonstrates the defect planes play a significant

role in restricting the flow of phonons when they try to cross these planes. Detailed orientation dependent experiments and thorough analyses of the thermal transport data are necessary and will be carried out to fully understand the roles of the defect planes.

CONCLUSIONS

Investigation on single crystals of reduced TiO$_2$ reveals interesting thermoelectric properties. Of particular importance is the role played by the defect planes in phonon blockade as evidenced by the anisotropy observed in the thermal conductivity in the directions parallel and perpendicular to the defect planes.

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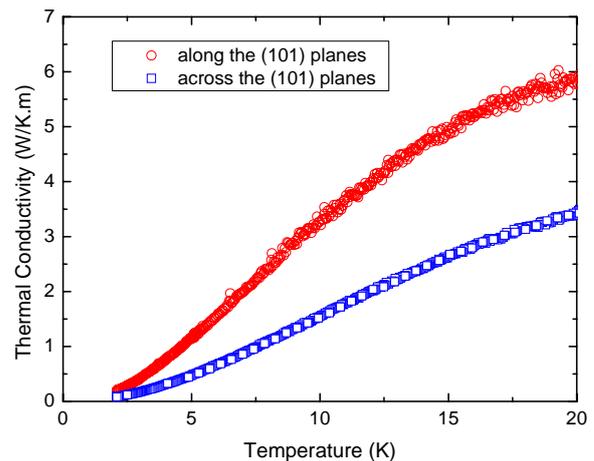
Figure 2. Thermal conductivity of a reduced rutile as a function of temperature measured in two directions: mainly along the (101) planes and across the (101) planes at right angle. The thermal conductivity along the (101) planes is higher than that across the (101) planes.