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Colossal positive Seebeck coefficient and low thermal conductivity in reduced TiO₂

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Abstract

Reduced (oxygen deficient) single crystal TiO₂ exhibits a very large positive Seebeck coefficient S at low temperature. S as large as $60\,000\ \mu\text{V K}^{-1}$ was observed near 10 K for the least reduced sample, which gives a thermoelectric power factor of $170\ \mu\text{W K}^{-2}\text{ cm}^{-1}$. This value is about four times higher than the power factor of Bi₂Te₃-based materials near room temperature. As the temperature increases the Seebeck coefficient becomes negative. The magnitude of the room temperature Seebeck coefficient, thermal conductivity and electrical resistivity decrease with the reduction of the samples. The thermal conductivity is as low as $0.83\ \text{W K}^{-1}\text{ m}^{-1}$ for the heavily reduced sample at 390 K due to phonon scattering by defect planes. The colossal Seebeck coefficient found in the materials is discussed in terms of the phonon drag of the holes.

(Some figures in this article are in colour only in the electronic version)

High Seebeck coefficient and electrical conductivity and low thermal conductivity are required of the advanced thermoelectric materials for power generation and cooling [1–3] which have gained renewed interest due to the needs for alternative energy resources and technology. Recent investigations by Japanese groups [4–7] have brought to light the importance of TiO₂ in thermoelectric applications. When the oxygen content is appropriately reduced, TiO₂ exhibits a promising figure of merit for thermoelectric applications. According to Tsuyumoto *et al* [4], TiO_x ($x = 1.86\text{--}1.94$), with orthorhombic structure, exhibits a Seebeck coefficient in the range of -60 to $-518\ \mu\text{V K}^{-1}$ between 25 and 70 °C. They estimated that the figure of merit, ZT , ranges from 0.0013 to 0.195 for these samples. A second report [5] showed that the magnitude of the Seebeck coefficient of TiO_{1.1} changes from $380\ \mu\text{V K}^{-1}$ at 300 °C to $1000\ \mu\text{V K}^{-1}$ at 950 °C. The thermal conductivity of TiO_{1.1} is $1.26\ \text{W K}^{-1}\text{ m}^{-1}$ at 300 °C, and it also increases with temperature. Introducing oxygen vacancies decreases both the thermal conductivity and Seebeck coefficient in TiO₂ [8, 9]. At the same time, the electrical resistivity decreases drastically due to the increase in the carrier concentration in the reduced

samples. The figure of merit, ZT , reaches as high as 1.64 at 800 °C, although these data are disputed by the report of He *et al* that shows a somewhat lower ZT [10]. The low thermal conductivity of microcrystalline thin films of TiO₂ was explained in terms of a glass like structure of the films [11].

It has been known for a long time that the Seebeck coefficient of rutile TiO₂ could be very large. At room temperature, values of $500\text{--}1000\ \mu\text{V K}^{-1}$ can be expected [8, 12]. Large negative Seebeck coefficients of -1000 to $-200\,000\ \mu\text{V K}^{-1}$ have been observed at low temperatures in rutile and Nb-doped rutile due to phonon drag [8]. The Seebeck coefficient is typically negative due to the oxygen vacancies and/or Ti interstitials commonly present in the reduced samples.

We have carried out an investigation on the thermoelectric properties of reduced (oxygen deficient) single crystal rutile TiO₂, which exhibit colossal positive Seebeck coefficients at low temperature that may be exploited for cryogenic thermoelectric device applications. The change of sign is due to the change of the predominant carriers from electrons to holes, and the large positive thermoelectric power may be attributed to phonon drag of the holes. A significant reduction in the thermal conductivity was observed originating from

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the phonon scattering by the defect planes of the reduced rutile.

Single crystals of rutile TiO_2 were purchased from MTI Corporation. The samples were annealed at temperatures ranging from 750 to 1170 °C. Each annealing was carried out in an H_2 flow and for a duration of 5 h. The thermoelectric properties of the samples were measured with a Quantum Design physical property measurement system (PPMS) from 10 to 400 K. The measurements were done with the heat and electrical current flow perpendicular to the (101) plane of the tetragonal lattice of the rutile. The dimension of the single crystals was 4 mm × 4 mm × 13 mm.

For the series of single crystal TiO_2 samples annealed in hydrogen at temperatures ranging from 750 to 1170 °C, the thermal conductivity κ decreases with the annealing temperature and, thus, the reduced oxygen content. The value of κ at 390 K decreases from 6 to 9 $\text{W K}^{-1} \text{m}^{-1}$ for the slightly reduced (annealed at 750 °C) sample to 0.83 $\text{W K}^{-1} \text{m}^{-1}$ for the heavily reduced sample (annealed at 1170 °C) (see figure 1). The small κ found in the heavily reduced samples suggests that phonon scattering by point defects and defect planes plays an important role in restricting the heat flow [13, 14]. Defect planes are characteristic of heavily reduced rutile of the Magnéli phase $\text{Ti}_n\text{O}_{2n-1}$ [14], where large concentrations of oxygen vacancies and/or Ti interstitials condense into platelets that are removed from the rutile structure, resulting in Magnéli shear planes. The analysis of the temperature dependence of κ at the very low temperatures indicates such scattering mechanisms. The inset to figure 1 shows the low temperature values of κ for the sample annealed at 1170 °C. At the very low temperature of our measurements, κ follows a $T^{1.77}$ dependence (as shown in figure 1, inset). This is slower than the T^3 behavior expected for phonon scattering by defect planes, which follows the same temperature dependence as the heat capacity [8, 15], but is influenced by the fact that data were not taken at temperatures lower than 10 K. All other samples show a T^ν ($\nu < 1$) dependence over the same temperature range.

Also shown in figure 1 is the annealing temperature dependence of the Seebeck coefficient S and electrical resistivity ρ measured at 390 K. S is negative except at very low measuring temperatures (as will be discussed below). Its magnitude decreases with increasing annealing temperature. ρ also decreases as the annealing temperature increases. Such changes in both S and ρ are attributed to the increase in the electron carrier concentration with the annealing temperature. The thermoelectric figure of merit, ZT , at 390 K increases with the annealing temperatures. It increases from 0.002 to 0.0085 when the annealing temperature changes from 780 to 1170 °C. The limited reduction in S and the much smaller κ and ρ of the reduced rutile lead to the overall improvement of thermoelectric performance.

Figure 2 shows the temperature dependence of κ , S and ρ of the sample annealed in hydrogen at 1100 °C. The thermal conductivity κ initially increases with T at low temperature, due largely to defect plane scattering, as discussed earlier, and reaches a maximum, where umklapp scattering and scattering from point defects and impurities

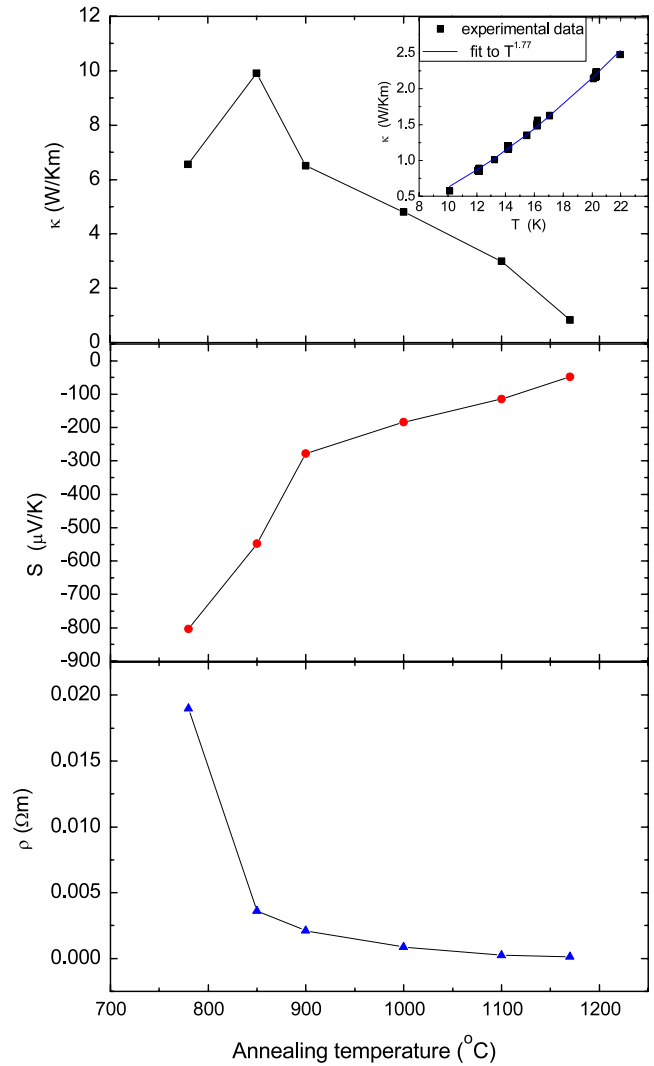


Figure 1. Thermal conductivity, Seebeck coefficient, and electrical resistivity at $T = 390$ K for single crystal reduced rutile TiO_2 as a function of the annealing temperature. The inset shows the experimental data for κ and the fit to $T^{1.77}$ at low temperature for the heavily reduced sample annealed at 1170 °C.

play a large role. As the temperature increases further, phonon–phonon scattering becomes dominant, and κ decreases with increasing T . The values of κ , S and ρ at 390 K are 3.0 $\text{W K}^{-1} \text{m}^{-1}$, $-114 \mu\text{V K}^{-1}$ and 0.00025 Ωm , respectively.

The Seebeck coefficient S changes its sign to positive values for $T < 28.5$ K, reflecting a change of the predominant carriers from electrons to holes. This indicates that the activation energy of minority carriers (holes) is lower than those of the majority carriers (electrons). Possible acceptors in the samples are impurities, e.g., Al [16]. Indeed, electron probe microanalysis has detected the presence of 0.08 at.% of Al in the annealed samples. The behavior of the sample annealed at 1100 °C in figure 2 is typical for all the samples, although the temperature at which this change of sign occurs varies from 21 to 23 K for the slightly reduced samples to 47 K for the heavily reduced sample. This trend is probably due to the changes in the energies of the impurity/defect levels as the samples are progressively reduced. As a matter of

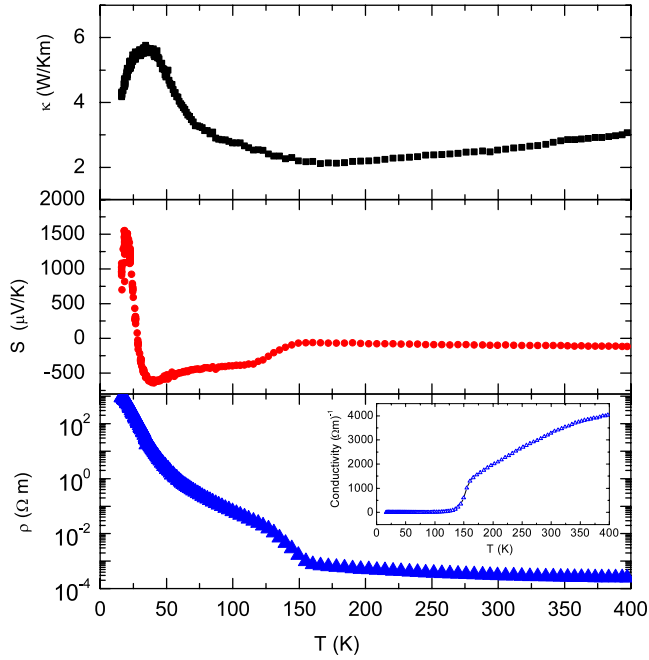


Figure 2. Thermal conductivity, Seebeck coefficient and electrical resistivity as a function of temperature of single crystal rutile TiO_2 reduced at 1100°C . Inset: electrical conductivity of the sample.

fact, we observed metal–insulator transitions from the metallic behavior at high temperature to the polaron transport at low temperature [17, 18], as shown in the electric conductivity versus temperature curve (see figure 2, inset). The transition temperature occurs at 40, 51, 55, 58, 144 and 150 K for samples annealed at 780, 850, 900, 1000, 1100 and 1170°C , respectively. The transition temperatures of the last two samples coincide with those of $\text{Ti}_n\text{O}_{2n-1}$ [17, 18] and suggest they are substantially reduced. As the systems make the transition to the polaron hopping regime, a relatively large negative S is observed, which is followed by the sign change at lower temperatures.

What is also interesting is that we have observed a colossal positive Seebeck peak at lower temperatures. Figure 3 shows the value of the Seebeck peak S_{max} as a function of the annealing temperature. For the sample annealed at 1100°C , S_{max} is about $1500 \mu\text{V K}^{-1}$ and occurs near 20 K. S_{max} increases with decreasing annealing temperature and is about $56000 \mu\text{V K}^{-1}$ for the sample annealed at 780°C (see figure 3, inset). Also shown in figure 3 is the resistivity at S_{max} as a function of the annealing temperature. It actually increases as the samples are progressively reduced, opposite to what is seen at high temperatures. However, this trend correlates well with the metal–insulator transition discussed above. As the transition temperature moves toward higher temperature with the annealing, the samples become more resistive at low temperature in the polaron regime.

The origin of this colossal positive S is most likely due to the phonon drag effect of the holes. Phonon drag of electrons has been interpreted as the cause for the large negative Seebeck S observed in rutile and Nb-doped rutile [8]. The phonon

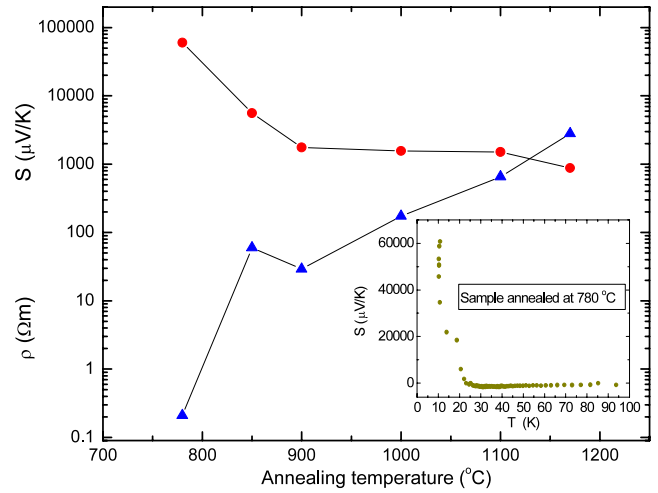


Figure 3. Maximum Seebeck coefficient and electrical resistivity at S_{max} (plotted on the same scale) as a function of the annealing temperature for single crystal reduced rutile TiO_2 . The inset shows the Seebeck coefficient as a function of temperature for the sample annealed at 780°C .

drag is essentially the effect in which carriers are preferentially scattered by the phonons in the direction of the heat flow. The phonon drag contribution to the Seebeck coefficient can be expressed as $S_{\text{ph}} = v^2\tau f/\mu T$, where v is the sound velocity, τ the phonon relaxation time, μ the mobility of the charge carriers, and f the fraction of carriers’ momentum that is transferred to the phonons [19]. At low temperatures, S_{ph} follows the behavior of the heat capacity C_V [20]. Indeed, the Seebeck peak S_{max} occurs at a temperature where C_V starts to increase drastically, which is $\sim 0.1\theta_D$ (θ_D : Debye temperature). θ_D is $450\text{--}780$ K for rutile TiO_2 [21] and S_{max} occurs at $10\text{--}30$ K. In comparison to the well known phonon drag system of bismuth [22], which has a Debye temperature of 119 K, the Seebeck peak is located at about $2\text{--}4$ K. A clear scaling between θ_D and the Seebeck peak temperature can be seen for the two systems. The colossal Seebeck coefficient decreases rapidly with increasing temperature. This is due to the reduced relaxation time τ for the long wavelength phonons, which interact with the electrons/holes, as a result of the increase in the carrier concentration. A peak at low temperature is characteristic of a phonon drag contribution to the Seebeck effect [19, 22]. When comparing samples annealed at different temperatures, the smaller τ , due to the defect plane scattering in the heavily reduced samples, leads to a smaller Seebeck coefficient from phonon drag. As discussed earlier, we did observe very large negative S just above the temperature at which it changes sign. The colossal positive S suggests there is a large phonon drag effect for the holes, as well as for the electrons. S_{max} found for holes is several times greater than that for electrons in rutile, but is less than that for Nb-doped rutile [8]. It is noticed that S_{max} for the slightly reduced samples occurs at about $10\text{--}15$ K, the same temperatures at which negative S_{max} was found for electrons in [8]. The phonon drag peaks of both holes and electrons occur at about the same temperature for other materials, for example bismuth [22], due to its correlation with C_V .

The power factor for the lightly reduced sample reaches $170 \mu\text{W K}^{-2} \text{cm}^{-1}$ near 10 K, which is about four times higher than Bi_2Te_3 -based materials near their operating temperatures. Our finding suggests that p-doped as well as n-doped rutile TiO_2 exhibit colossal Seebeck coefficient, which makes the material particularly attractive for device applications at low temperatures [22] because the same base materials can be used for the p and n legs of the thermoelectric converter, although further improvement in the ZT is needed. In addition to cryogenic applications, understanding its origin may help us tune and design materials that may have desirable features for various applications at higher temperatures. The low thermal conductivity, due to phonon scattering by the defect planes, is a unique feature of reduced rutile TiO_2 that should be further investigated and explored for applications. The best figure of merit ZT is about 0.0085 at 390 K, observed in the heavily reduced sample, and shows a tendency to increase with a further increase in temperature above 400 K.

Acknowledgments

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