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Major enhancement of the thermoelectric performance in Pr/Nb-doped SrTiO₃ under strain

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The electronic structure and thermoelectric properties of strained (biaxially and uniaxially) Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃ are investigated in the temperature range from 300 K to 1200 K. Substitutions of Pr at the Sr site and Nb at the Ti site generate n-type doping and thus improve the thermoelectric performance as compared to pristine SrTiO₃. Further enhancement is achieved by the application of strain, for example, of the Seebeck coefficient by 21% for Sr_{0.95}Pr_{0.05}TiO₃ and 10% for SrTi_{0.95}Nb_{0.05}O₃ at room temperature in the case of 5% biaxial strain. At 1200 K, we predict figures of merit of 0.58 and 0.55 for 2.5% biaxially strained Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃, respectively, which are the highest values reported for rare earth doped SrTiO₃. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4815928>]

Due to an increasing demand of renewable energy, thermoelectric materials nowadays are attracting much attention as they directly convert thermal energy into electrical energy. In particular, thermoelectric oxides are interesting because of their low manufacturing costs, environmental friendliness, nontoxic character, availability in nature, and high service temperatures.^{1,2} SrTiO₃, a cubic perovskite with a wide band gap of 3.2 eV, is a prototypical compound known for unusual properties such as superconductivity, quantum ferroelectricity, anomalous photoconductivity, high Hall mobility, and large n-type thermoelectric response.^{3,4} Due to its high dielectric constant, it is used in field effect transistors and electric field tunable capacitors.⁵ Pristine SrTiO₃ is not a good thermoelectric material due to its insulating nature and high thermal conductivity.⁶ However, charge carriers can be injected to enhance the thermoelectric behavior. The most frequently used techniques for carrier injection are doping, alloying, and the introduction of O vacancies.⁷ Such modifications usually generate new energy levels in the band gap. In general, the thermoelectric performance of a material can be evaluated in terms of the dimensionless thermoelectric figure of merit defined as $ZT = \frac{TS^2\sigma}{\kappa}$, where T is the absolute temperature, S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity.

To improve the thermoelectric response of doped SrTiO₃, various atomic substitutions and defects have been investigated experimentally and theoretically. Yamamoto *et al.*⁸ have put forward a compositional thermoelectric phase diagram, which includes the effective mass, the carrier relaxation time, and the thermoelectric power factor for 20% Nb-doped CaTiO₃, SrTiO₃, and BaTiO₃. In Ref. 6, a first principles calculation has been reported on the alteration of the electronic and transport properties for substitution of La at the Sr site as well as Nb and Ta at the Ti site. Moreover, Ohta *et al.*^{9,10} have measured thermoelectric properties of heavily La/Nb-doped SrTiO₃ at high temperature and have

found ZT values of 0.27 and 0.37 at 1000 K for 20% doping, respectively. The first principles calculations in Ref. 11 for Nb and V co-doped SrTi_{1-2x}Nb_xV_xO₃ with $x = 12.5\%$ and 25% have addressed the question how the introduction of spin polarization affects the thermoelectric behavior as compared to merely Nb-doped SrTiO₃. Moreover, it has been found that the addition of K₂Ti₆O₁₃ to Nb-doped SrTiO₃ gives rise to a maximal ZT value of 0.34 at 900 K.² The influence of O deficiency on the thermoelectric properties of SrTiO₃ has been studied in detail in Refs. 12–16.

Rare earth doped SrTiO₃ has attracted considerable attention, because the thermal conductivity is reduced while the electrical properties are maintained.^{17,18} Y, La, Sm, Gd, and Dy doping of SrTiO₃ has been studied by Zhang *et al.*,¹⁹ finding a maximal ZT of 0.22 at 800 K for Sr_{0.92}La_{0.08}TiO₃. Wang *et al.*²⁰ have reported that dual doping of La and Dy can significantly improve the thermoelectric properties. A maximal ZT value of 0.36 is obtained for La_{0.08}Dy_{0.12}Sr_{0.8}O₃ at 1076 K. It is expected that Pr-doped SrTiO₃ has a much lower thermal conductivity than this is the case for other dopants (Y, La, Sm, Gd, and Dy) due to the similar ionic radii of Pr and Sr. Recently, Kovalevsky *et al.*²¹ have found that Pr substitution at the Sr site increases the electrical conductivity, leading to an increase of the powerfactor. In general, the thermoelectric efficiency of a device can be enhanced by tuning the band gap by alloying or strain.^{22–24} From the above discussion, it is clear that substitutional doping in SrTiO₃ in fact can improve the thermoelectric performance, thus, forming a promising approach in thermoelectric technology. Alteration of ZT by strain is also an appealing idea, because strain develops naturally in epitaxial films due to lattice mismatch with the substrate. In this respect, it is surprising that so far no investigation has addressed doped SrTiO₃ under strain. To overcome this gap, we systematically substitute in the present study Pr on the Sr site and Nb on the Ti site and investigate the electronic structure and thermoelectric performance under both biaxial and uniaxial tensile strain.

We employ calculations within density functional theory, using the full-potential linearized augmented plane

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wave WIEN2K package.²⁵ The spin polarized generalized gradient approximation plus onsite interaction approach for the exchange correlation potential with onsite interactions of $U = 6$ eV for the Pr $4f$ orbitals and $U = 4$ eV for the Ti and Nb $3d$ orbitals is applied. Moreover, the spin orbit coupling is taken into account. The parameter $R_{mt}K_{max}$ (where K_{max} is the plane wave cut-off and R_{mt} is the smallest muffin-tin radius) controls the size of the basis. It is set to a safe value of 7, with $\ell_{max} = 12$ and $G_{max} = 24$. We use a $9 \times 9 \times 3$ k-space grid with 30 points in the irreducible wedge of the Brillouin zone. Self-consistency is assumed to be achieved for a total energy convergence of 10^{-5} Ry. Finally, the transport properties are calculated using semi-classical Boltzmann theory, as implemented in the BoltzTraP code,^{26,27} with 2000 k-points in the irreducible wedge of the Brillouin zone.

We start from the unit cell of cubic SrTiO₃ with the lattice constant 3.905 Å and space group 221 (Pm $\bar{3}$ m),³ because it has been reported that Sr_{0.95}Pr_{0.05}TiO₃ also exhibits a cubic structure.²⁸ For modeling, 5% Pr doping at the Sr site and 5% Nb doping at the Ti site, we construct $2 \times 2 \times 5$ supercells in which we replace either one Sr atom by Pr or one Ti atom by Nb. Substitution on the opposite sites (Pr on the Ti site and Nb on the Sr site) is chemically impracticable due to high differences in the ionic radii. In order to investigate the electronic structure, we have calculated the total and partial densities of states (DOSs) of Pr-doped and Nb-doped SrTiO₃ without strain as well as under 2.5% and 5% biaxial strain (with respect to the lattice parameters). We also address 2.5% uniaxial strain in both systems.

The total DOS in Fig. 1 shows that doping of 5% Pr changes the insulating behavior of SrTiO₃ into an n-type metal. This fact is due to a transfer of charge from Pr to the host system, which shifts the Fermi energy (E_F) into the conduction band. The n-type metallic nature is in agreement with the experimental results reported in Ref. 21. While the Ti $3d$ states cross E_F , the Pr $4f$ states do not appear in the

vicinity of E_F . The top of the valence band is dominated by the O $2p$ states (not shown). Under the application of 2.5% and 5% bi-axial strain, these O $2p$ states shift to higher energy and the gap between the valence and conduction bands decreases, see Fig. 1. The observed strong modification of the band gap with increasing strain plays a key role for the efficiency of thermoelectric devices.²⁹ The calculated Pr magnetic moment in the unstrained system amounts to $1.97 \mu_B$ and is entirely due to the $5f$ states, while all other states are virtually spin degenerate. By increasing the strain from 2.5% to 5%, the magnetic moment slightly increases from $1.98 \mu_B$ to $1.99 \mu_B$, respectively, which reflects a minor modification of the occupation of the Pr $5f$ states due to the fact that the application of strain enlarges the interatomic distances. However, these states appear far away from E_F and thus do not participate in the thermoelectric response of the material.

Nb-doped SrTiO₃ is addressed in Fig. 2, which shows a similar picture as obtained for the Pr-doped system. Extra charge due to the Nb dopant shifts E_F into the conduction band. The Ti $3d$ and Nb $4d$ states are partially occupied, which induces an n-type metallic character, in agreement with the experimental reports in Ref. 30 for SrTi _{x} Nb _{$1-x$} O₃ ($x > 0.1$). Again the top of the valence band is due to the O $2p$ states, which shift to higher energy under biaxial strain. The intermixing of the symmetry components of the Nb $3d$ states decreases, while the Ti $3d$ DOS remains similar to the unstrained system. Calculated total and partial DOSs of doped SrTiO₃ under 2.5% uniaxial strain along the long axis of the supercell are shown in Fig. 2. We find no significant change as compared to 2.5% biaxial strain. However, the intermixing between the symmetry components of the Ti $3d$ and Nb $4d$ states is reduced, which enhances the effective masses and, hence, the Seebeck coefficient.

The thermoelectric response of doped SrTiO₃ without and with biaxial and uniaxial strain is addressed in Fig. 3 for

FIG. 1. Total and partial (per atom) densities of states of Pr-doped SrTiO₃. Black lines indicate biaxial strain and red lines uniaxial strain.

FIG. 2. Total and partial (per atom) densities of states of Nb-doped SrTiO₃. Black lines indicate biaxial strain and red lines uniaxial strain.

the temperature range from 300 K to 1200 K. The Seebeck coefficient presented in the top row of the figure is negative in the whole temperature range for both systems, indicating that the majority charge carriers are electrons. For unstrained Nb-doped SrTiO₃ at 300 K, the Seebeck coefficient amounts to $-61 \mu\text{V/K}$, which is close to the experimental value of $-57 \mu\text{V/K}$ from Ref. 31. It is enhanced to $-68 \mu\text{V/K}$ under 5% biaxial strain. Similarly, we find at 300 K for unstrained Pr-doped SrTiO₃ Seebeck coefficients of $-60 \mu\text{V/K}$ without and $-76 \mu\text{V/K}$ under 5% biaxial strain. The absolute value of the Seebeck coefficient increases monotonically with the temperature in all cases due to the fact that the chemical

potential decreases.^{10,31} At elevated temperature, the slope becomes smaller and the curve saturates, indicating that there is a narrow conduction band near E_F , as confirmed by the band structure (not shown). The presence of this band is a result of the Pr and Nb doping, as it shifts E_F . At elevated temperature, the Seebeck coefficient thus loses its dependence on the temperature, where above 700 K the value for 2.5% uniaxial strain is always significantly larger than for the unstrained and biaxially strained systems. At 1200 K, we obtain $-150 \mu\text{V/K}$ for unstrained Pr-doped SrTiO₃ and $-147 \mu\text{V/K}$ for unstrained Nb-doped SrTiO₃. These values are enhanced to $-160 \mu\text{V/K}$ and $-158 \mu\text{V/K}$, respectively, under 2.5% uniaxial strain, which is due to higher effective masses, and thus, lower electrical conductivity. At high temperature, the Seebeck coefficient is higher for uniaxial than for biaxial strain because of a lower electrical conductivity. By the larger bond lengths under strain, the intermixing between the Ti 3d and Nb 4d symmetry components decreases. The higher Seebeck coefficients of the uniaxially strained systems are in line with this scheme.

Under strain, the lattice thermal conductivity is, in general, lower than without strain, because point defects due to the Pr and Nb substitutions enhance the phonon scattering. Furthermore, the distortion of the lattice and weakening of the Ti-O bonds under strain induce additional phonon scattering, resulting in a further reduction. At high temperature, the lattice contribution to the thermal conductivity is negligible (at least one order of magnitude smaller than the electronic contribution), because of the strong phonon scattering. Our calculated electronic thermal conductivity in the temperature range from 300 K to 1200 K is shown in Fig. 3. At 1200 K, we find for unstrained Pr-doped SrTiO₃ a value of $\kappa = 2.4 \text{ Wm}^{-1}\text{K}^{-1}$, which is close to the experimental value of $2.6 \text{ Wm}^{-1}\text{K}^{-1}$ in Ref. 21, confirming the accuracy of our predicted ZT at high temperature. The relaxation time τ is taken from Ref. 8.

Results for $Z = \frac{S^2 \sigma}{\kappa}$ are presented in the lower row of Fig. 3. We find an increase with the biaxial strain, always

FIG. 3. Thermoelectric properties of Pr-doped (left) and Nb-doped (right) SrTiO₃, where S is the Seebeck coefficient, κ is the thermal conductivity, τ is the relaxation time, and Z is the figure of merit.

showing a broad maximum around room temperature. For 2.5% and 5% biaxially strained Pr-doped SrTiO₃ at 300 K, we obtain values of $0.62 \times 10^{-3} \text{ K}^{-1}$ and $0.68 \times 10^{-3} \text{ K}^{-1}$, respectively, and for Nb-doped SrTiO₃ values of $0.55 \times 10^{-3} \text{ K}^{-1}$ and $0.52 \times 10^{-3} \text{ K}^{-1}$. Although the room temperature Z is smaller for 2.5% uniaxial strain than for the same amount of biaxial strain for both systems, we find a larger value at high temperature (above 700 K). For 5% biaxial strain, the maximum of Z appears around room temperature. However, for higher temperature, the values are smaller than for the uniaxially strained systems. For rare earth doping, a maximal $Z = 0.38 \times 10^{-3} \text{ K}^{-1}$ at 573 K has been reported for Dy-doped SrTiO₃ in Ref. 32. At the same temperature, we calculate $Z = 0.55 \times 10^{-3} \text{ K}^{-1}$ for Pr-doped SrTiO₃, which is further enhanced to $0.65 \times 10^{-3} \text{ K}^{-1}$ under 2.5% biaxial strain. Our calculated Z at 1100 K is $0.50 \times 10^{-3} \text{ K}^{-1}$ and thus 10 times larger than the values reported for other rare earth (La, Sm, Gd, and Dy) dopants at the same temperature.³² An increasing Z value at high temperature under uniaxial strain is also obtained for Nb-doped SrTiO₃. At 300 K without strain, we obtain $0.47 \times 10^{-3} \text{ K}^{-1}$, which is enhanced to $0.55 \times 10^{-3} \text{ K}^{-1}$ by 2.5% biaxial strain. Similarly, at high temperature (1200 K), we have $Z = 0.48 \times 10^{-3} \text{ K}^{-1}$ under uniaxial strain. We obtain for 2.5% uniaxially strained Pr-doped SrTiO₃ $ZT = 0.60$ and for Nb-doped SrTiO₃ $ZT = 0.58$ at 1200 K, while for 2.5% biaxially strained Pr-doped SrTiO₃, we have $ZT = 0.58$ and for Nb-doped SrTiO₃ $ZT = 0.55$ at 1200 K. These are the highest values ever reported for doped SrTiO₃ at this temperature.^{9,21,32} The outstanding properties of both systems are due to fact that strain increases the Seebeck coefficient and decreases the thermal conductivity, as discussed above.

In conclusion, we have investigated the electronic structure and thermoelectric properties of Pr/Nb-doped SrTiO₃, focussing on the effects of biaxial and uniaxial strain. We find that the substitution of Pr and Nb on the Sr and Ti sites, respectively, transforms insulating SrTiO₃ into an n-type metal. Comparing biaxial and uniaxial strain of the same amount, we find no significant difference in the calculated Pr 4*f*, Nb 3*d*, and Ti 3*d* DOSs of Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃. Under strain, the intermixing between the symmetry components of the Ti 3*d* and Nb 4*d* states is reduced, which contributes to the high Seebeck coefficient. For 5% biaxially strained Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃, we obtain at room temperature $S = -76 \mu\text{V/K}$ and $S = -68 \mu\text{V/K}$, respectively. These values are larger than the corresponding results for the unstrained systems ($-60 \mu\text{V/K}$ and $-61 \mu\text{V/K}$). At 1200 K, we find for 2.5% uniaxially strained Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃ high figures of merit of 0.60 and 0.58, respectively, and for 2.5% biaxial strain values of 0.58 and 0.55. This constitutes a significant enhancement over any previously reported value for rare earth doped SrTiO₃. The Seebeck coefficient and figure of merit first increases under strain due to larger effective masses (elongated bonds) but start to decrease again for large strain. Our results thus demonstrate that

moderately strained Sr_{0.95}Pr_{0.05}TiO₃ and SrTi_{0.95}Nb_{0.05}O₃ are excellent candidates for high temperature n-type thermoelectric devices.

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