Enhanced effective mass in doped SrTiO$_3$ and related perovskites

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The effective mass is one of the main factors determining the Seebeck coefficient and electrical conductivity of thermo-electrics. In this ab-initio LDA-GGA study the effective mass is estimated from the curvature of electronic bands by one-band-approximation and is in excellent agreement with experimental data of Nb- and La- doped SrTiO$_3$. It is clarified that the deformation of SrTiO$_3$ crystals has a significant influence on the bandgap, effective electronic DOS- mass and band- mass, but the electronic effect due to the e$_{2g}$-$d$ band flattening near the $\Gamma$-point due to Nb -doping up to 0.2 at% is the main factor for the effective mass increase. Doping of La shows a linear decrease of the effective mass; this can be explained by the different surroundings of A- and B-sites in perovskite. Substitution with other elements such as Ba on the A-site and V on the B-site in SrTiO$_3$ increases the effective mass as well.

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Introduction

Heavy doping with Nb or La turns SrTiO$_3$ into an n-type degenerate semiconductor and a rather large thermoelectric figure of merit of 0.34 at 1000K is achieved$^{12}$, in superlattice structures even higher values due to the confinement in the two-dimensional electron gas. Further improvement requires the increase of the effective mass as the most important factor$^{10}$ for the Seebeck coefficient and conductivity. This paper compares the experimentally determined values for the effective electron mass with those obtained from ab-initio calculations. In a previous study$^1$ an effective electron mass of $m^*/m_0=7.2$ (free electron mass) for SrTiO$_3$ was determined from thermoelectric data, which increase with the Nb -doping concentration up to 0.2% and decrease with the La- doping concentration, and is consistent with $m^*/m_0=1.8$ and 1.9 for reduced for SrTiO$_3$ was measured. For very high Nb-concentrations of 5% at low temperatures $m^*/m_0=15$ was determined$^{11}$ by interpretation of experimental data, while far smaller values of $m^*/m_0=1.17$ and 1.51 were reported for pure and La-doped SrTiO$_3$. $m^*/m_0$ was obtained by ab-initio calculation for SrTiO$_3$. Also spectroscopic measurements obtained an effective mass of $m^*/m_0=5.0$ for SrTiO$_3$, and $m^*/m_0=3.3$ for SrVO$_3$. Assuming that effective mass values $m^*/m_0$ obtained by different experimental measurement methods, like Hall-mobility $\mu$, conductivity $\sigma$ and Seebeck $S$ measurements, are consistent, the discrepancy can be explained by the Kane model$^{7}$ which states that there is an increase of the effective mass $m^*/m_0$ with charge carrier concentration $n$, or in other words the bare electron mass$^{11}$ from bandstructure increases due to polaron effects. The dependence of these macroscopic properties $\mu, \sigma$ and $S$ on the microscopic parameters $m^*/m_0, n$ and relaxation time $\tau$ has been proven by a semi-empirical theory$^{30}$ solving the Fermi-integral. This approach for calculating the thermoelectric properties from $m^*/m_0$ was used in this paper and allows common ab-initio software$^{21,22}$ to be used straight-forwardly. Indeed such bandstructure calculations of the effective masses of heavy and light electrons and their average $m^*/m_0$ have been successfully performed for III-V semiconductors with excellent agreement with experimental data.$^{13}$ Other approaches have been performed, like calculating the thermopower directly from orbital interactions by solving Heikes’ formula in the Hubbard model shown for the example of SrCoO$_3$.\footnote{Ab-initio simulations on SrTiO$_3$,\cite{14,25-31} usually show a smaller band-gap than the experimental 3.2eV, but the difference vanishes, when a suitable self-energy $U$ is used (LDA+$U$ calculations); nevertheless the main features of the bandstructure remain unchanged. The density-of-states (DOS) shows a remarkable steep increase at the valence band maximum (VBM) and the conduction band minimum (CBM) due to highly populated O-p- and Ti-$e_{2g}$-states.\cite{26,30} Oxygen vacancies introduce a donor level a few 100meV below the CBM.\cite{28,32} In general, large effective masses are caused by electron correlation effects near a metal-insulator transition (MIT).\cite{15,35} In the case of La -doping, the band- insulator Sr$_{1-y}$La$_y$TiO$_3$ with $y=0$ becomes metallic near $\tau=0.1$ and again an insulator of Mott-type near $\tau=0.9$.\cite{35} La occupies the Sr -site, and Nb the Ti -site, and in both cases the electron concentration increases linearly with the doping level, when the oxygen concentration is kept constant.\cite{15,36} Nb-doping increases the valence of the Ti-site from 4+ to 5+, so that oxygen reduction becomes favorable and both defects\cite{37} can only treated as independent for small concentrations. It is well accepted, that in these n-type Ti- perovskites only the electron conductivity needs to be considered, not holes. Furthermore, compared to other perovskites for lightly doped SrTiO$_3$ no clear evidence has yet been found for magnetic ordering, octahedron tilting or Jahn-Teller effects, although at highly doped SrTiO$_3$ these might occur.\cite{29,35,38}}

The goal of this paper is to find a reliable ab-initio method to calculate the effective mass which fits to experimental data of conductivity and Seebeck- coefficient measurements for both, doped and oxygen deficit SrTiO$_3$. First, the dependence of thermoelectric properties on the effective mass is shown. Then, the calculation method is explained, focusing especially how the effective mass from the electronic band structure and that from the density of states are related. The results of the bandstructure features and effective mass calculation are presented for several non-stochiometric, deformed, doped variants of SrTiO$_3$ as well as related substitutional perovskites. Finally, the influences of the different phenomena are summarized. In subsequent papers, the effective mass for layered perovskites was investigated.\cite{35}
2. Calculation method

According to the equations in ref. 18, the Seebeck coefficient can be calculated phenomenologically by solving the Fermi integral if the effective mass $m^*$, the carrier concentration $n$, and the scattering factor $r=0.5$ are known. For calculation of the electrical conductivity $\sigma$ the relaxation time for electron-phonon-scattering $\tau$ is also required, which was found to be independent of La- and Nb-doping for SrTiO$_3$, $\tau=18$ fs at $T=300K$. In previous calculations by using an empirical method the parameters $m^*$, $n$ were varied over wide ranges and the resulting negative Seebeck coefficient $-S$, and conductivity $\sigma$ showed excellent agreement to experimental data.

The Seebeck coefficient $-S$ increases steeply when the effective mass increases from $m^*/m_0=1$ to 5 and moderately above that value, while the conductivity decreases due to smaller mobility. The resulting power factor $S^2\sigma$ as a function of $m^*$ and $n$ shows that the decrease in mobility by increasing $m^*$ is almost compensated by the gain in $S^2$, while the charge carrier concentration indeed requires optimum adjustment between the insulating and metallic behavior. Such calculations can be used to estimate $m^*$ and $n$ from $S$ and $\sigma$.

Room temperature data on $m^*$ of doped SrTiO$_3$ are summarized in Table 1 and show good agreement among each other.

The ab-initio software program Vasp based on the density-functional theory (DFT) with generalized gradient approximation (GGA) was used in this study with a pseudo-potential cutoff-energy of $\varepsilon_{cut}=\approx380eV$. The Wien2k code which uses the linear augmented plane-wave (LAPW) method leads to the same results, respectively. Both ab-initio codes include the relativistic approximation and the spin-orbit interaction and show excellent agreement among each other.

In order to prove this, the DOS masses $m_{DOS}$ in the following called effective band mass, was estimated in the one-band-approximation from the curvature of each band $i$ at each k-space $j$ (usual Γ point); or in other words, parts of the band mass $m_{B,i}$ for each band $i$ at each j-point, conduction band minimum (CBM) or valence band maximum (VBM), were fitted by parabolic curves as

$$ m_{B,i,j} = \frac{2}{\hbar^2} \frac{d^2E_{i,j}}{dk^2} $$

(1), with Planck's constant $\hbar$. The averages over $j$, namely heavy (h) and light (l) parts from the same band $i$ were calculated according to the following formula from ref. 41 yielding to the effective band mass

$$ m_{B,i} = \left( m_{B,i,h}^{3/2} + m_{B,i,l}^{3/2} \right)^{2/3} $$

(2).

By comparison with experimental data and the above mentioned observation 1,2 that in n-semiconductors only electrons are relevant for electric conductivity, it was found that the mass from electrons with the lowest energy in the conduction band determines the electrical transport properties and is equivalent to the effective mass $m^*$ in Drude's equation, which is measured in experiments, can be calculated from

$$ m' = m_e^* = m_{B,i} $$

(3) with $i=1$ (minimal conduction band). The main statement of this paper is that formulas (1-3) allow the estimation of effective mass $m^*$ measured in experiments by ab-initio bandstructure calculations from $m_{B,i}$. The values for $m^*$ derived by this method showed good agreement with literature values of the effective masses for both electrons and holes at all significant reciprocal space points of the III-V semiconductors GaN, GaP, GaAs, InAs and InAs, as well as ZnO and TiO$_2$.

The experimental thermoelectric properties of doped SrTiO$_3$ are summarized in Table 1.

| Doping  | Carrier concentration $n$ | Effective mass $m^*/m_0$ | Seebeck coefficient $S$ | Conductivity $\sigma$ | Ref. |
|--------|--------------------------|--------------------------|-------------------------|----------------------|-----|
| La 0.005 | 0.5                      | 6.6                      | -420                    | 54                   | 1   |
| La 0.07  | 6.8                      | 6.0                      | -150                    | 1000                 | 1   |
| Nb 0.01 | 1.5                      | 7.3                      | -330                    | 95                   | 1   |
| Nb 0.02  | 3.7                      | 7.7                      | -240                    | 353                  | 1   |
| La 0.02  | 4.0                      | 4.2                      | -200                    | -                    | 3   |
| La 0.02  | 3.7                      | 4.5                      | -260                    | 433                  | 15  |

*) Instead of the published value of 1.51 in ref. 15, a value of $m^*/m_0=4.5$ calculated by the equations in ref. 20 by relating $n$, and $m^*$ to $S$, and $\sigma$ leads to data consistency.

FIG 1. Effective mass estimated from fit parables (bright lines, eq. (1)) to the calculated (dark lines) band structure of the conduction band of SrTiO$_3$, near the Γ-point in Γ−Δ-direction.
 Dependences of yielding an average value according to eq. (2) of compared to the mentioned that to equation (5) and that derived from the density of states by equations (1,2) show excellent agreement to each other. However, it should be mentioned that m_{DOS} is not related to the experimentally determined effective mass m^*, as can be seen for example, on the opposite dependences of m^* and m_{DOS} on the Nb-content for doped SrTiO_3 described in the last section (fig. 5). This means, that unfortunately the less costly calculation of the density- of- states cannot be used to estimate effective mass m^* relevant for electric conduction properties, only that from band structure calculations can be used.

The experimental data of m^*/m_0 for doped SrTiO_3 are summarized in Table 1 and vary from 4.2 to 7.2. The calculations for pure SrTiO_3 show a value of m_{DOS}/m_0=4.4 for heavy electrons around the Γ-point in the Γ−∆ (100) direction, while the masses in the Γ−Σ (110) or Γ−Λ (111) directions are smaller (m_{DOS}/m_0=1.1), yielding m^*/m_0=4.8 which is in good agreement with experimental values1,3,13 (Table 1) When comparing calculations of a single unit cell and a 2x2x2 supercell of undoped SrTiO_3 the band- curvature, and hence the effective mass, is unchanged; the only difference is that the degeneracy is suppressed. While m_{DOS}/m_0=4.4 is obtained when fitting in the vicinity of the Γ-point (Fig. 1 (a)), a larger effective mass of m_{DOS}/m_0=6.6, resulting in m^*/m_0=6.8, is obtained (Fig. 1 (b)), when the fit is extended towards X including non-parabolic deviations, namely a small hump in the difference between the band and the parabolic fit, which appears in highly-accurate Vasp calculations only. In the following the parabolic values without the hump were used, but note that this non-parabolic behavior is one of factors explaining the large effective mass of 7.2 in the experiment. Further factors, such as lattice expansion, oxygen vacancies and doping as described later, might be the reason for their small effective mass.

Effective masses of distorted SrTiO_3 lattices

3. Results

Effective masses of distorted SrTiO_3 lattices

The calculated electronic band structure of SrTiO_3 shows excellent agreement with literature data1,15,17 with its slightly indirect gap band due to the higher valence band level at the Σ and M points compared to the Γ point. As most other researchers did14,16, we will in the following renounce the plot of the M-R section15. When the SrTiO_3 lattice is isotropically expanded (a,b,c=1.1a) (Fig. 2(a)) the lowest conduction band near the Γ point in the Δ(100) direction shows a smaller curvature, and hence the highest effective mass m^*/m_0=5.0, compared to 1.2 in Σ-direction and 1.3 in the Λ-direction, yielding an average value according to eq. (2) of m^*/m_0= 5.8. While the band structure of the isotropic expanded lattice does not change its morphology (Fig. 2(a)), an orthorhombic distortion (a=0.375nm, b=0.4066nm) shows a suppression of the degeneracy, in other words band splitting occurs (Fig. 2(b)). Although there is still a conduction band (i=3 counting from E_{GAP}) with a large effective mass 3.6, the lowest band in energy (i=1, see Table 2) now has a strong curvature, which leads to m^*/m_0=0.3. The three-dimensional plot in Fig. 3 summarizes the dependence on the lattice constants a, b, as shown in the upper left inset, while along A-B the volume is constant, as shown in the right inset. The lattice constant c was determined by c=a·b/a_0. The distortion of epitaxially grown thin films with a and b adjusted to the substrate, leaving c unchanged, would be an intermediate case (middle inset). The band-gap decreases steeply from 3.2eV of undeformed SrTiO_3 to 2.5eV when the lattice is expanded (a,b,c=1.03a), while the effective mass increases to 8.2 (see also Table 2). The band-gap decrease can also be recognized in the density- of- states plot as a function of lattice constants in Fig. 4(a). This plot also clearly shows the increase in m_{DOS} due to steeper envelopes (see also Table 2). Fig. 3 and 4(b) are symmetric along the axis A-A. When the lattice is
distorted in orthorhombic shape, the bandgap is almost unchanged as derived from the DOS (Fig. 4(b)). Also the band effective mass is unchanged \((m^*/m_0=4.5)\) as seen in Fig. 4(d). The effective mass \(m_{\text{DOS}}\) decreases, because band

Table 2 Calculated effective masses \(m_{\text{DOS}}, m_{\Gamma_{IJ}},\) and \(m^*\) of doped or strained SrTiO\(_3\). Values are in units of the free electron rest mass \(m_0\). The values for \(\Gamma-\Sigma\), or \(\Gamma-\Lambda\) are summarized in one column, because they are almost identical.

| Composition                  | Valence band | Conduction band |
|-----------------------------|--------------|-----------------|
|                             | \(m_{\text{DOS}}\) | \(m_{\Gamma_{IJ}}\) | \(m^*\) | \(m_{\text{DOS}}\) | \(m_{\Gamma_{IJ}}\) | \(m^*\) |
| SrTiO\(_3\) near \(\Gamma\) (Fig. 1(a)) | 4.59 | 3.5 | 2.8 | 9.8 | 3.53 | 4.4 | 1.1 | 4.8 |
| SrTiO\(_3\) \(\Gamma\)-extended (Fig. 1(b)) | 4.59 | 3.5 | 2.8 | 9.8 | 3.53 | 6.6 | 1.1 | 7.5 |
| SrTiO\(_3\), \(a, b, c=1.1a_0\) | 5.17 | 3.5 | 2.7 | 9.4 | 5.17 | 6.3 | 1.3 | 8.2 |
| SrTiO\(_3\), \(a, b, c=0.9a_0\) | 4.81 | 3.5 | 2.7 | 9.4 | 2.81 | 2.9 | 1.0 | 2.9 |
| SrTiO\(_3\), \(a=0.9a_0, b=1.1a_0, i=3\) | 4.96 | 3.5 | 2.8 | 9.8 | 2.83 | 3.6 | 0.9 | 3.4 |
| SrTiO\(_3\), \(a=0.9a_0, b=1.1a_0, i=1\) | 4.96 | 3.5 | 2.8 | 9.8 | 2.83 | 0.3 | 0.9 | 0.3 |
| SrTiO\(_2\) | 3.62 | 10 | 2.7 | 27 | 2.9 | 4.4 | 1.8 | 7.7 |
| SrTiO\(_2\) \(_{0.92}\) | 2.60 | 8.0 | 2.05 | 16 | 2.23 | 2.0 | 1.6 | 7.2 |
| SrTi\(_{0.88}\)Nb\(_{0.12}\)O\(_3\) | 3.25 | 10 | 2.7 | 27 | 2.17 | 6.0 | 1.1 | 6.3 |
| SrTi\(_{0.88}\)Nb\(_{0.25}\)O\(_3\) | 2.96 | 4.0 | 3.0 | 12 | 2.07 | 0.2 | 1.0 | 0.2 |
| SrTi\(_{0.88}\)Nb\(_{0.12}\)O\(_2\) \(_{0.96}\) | 3.99 | 0.6 | 1.6 | 0.9 | 3.99 | 4.0 | 1.2 | 4.8 |
| SrTi\(_{0.88}\) Nb\(_{0.12}\) O\(_2\) \(_{0.92}\) | 2.96 | 0.4 | 1.5 | 0.6 | 3.5 | 8.0 | 1.3 | 7.8 |
| Sr\(_{0.88}\)La\(_{0.12}\)TiO\(_3\), \(i=1, a=a_0\) | 4.76 | 10 | 2.7 | 27 | 3.74 | 3.6 | 1.1 | 3.7 |
| Sr\(_{0.88}\)La\(_{0.12}\)TiO\(_3\), \(i=1, a=0.99 a_0\) | 4.85 | 4.0 | 1.4 | 4.9 | 3.81 | 3.6 | 1.2 | 4.3 |
| Sr\(_{0.75}\)La\(_{0.25}\)TiO\(_3\), \(i=2, a=0.98 a_0\) | 4.42 | 6.0 | 2.6 | 13 | 3.98 | 3.2 | 1.3 | 4.2 |
| Sr\(_{0.75}\)La\(_{0.25}\)TiO\(_3\), \(i=1, a=0.98 a_0\) | 4.42 | 6.0 | 2.6 | 13 | 3.98 | 0.2 | 0.7 | 0.2 |

FIG. 3. (a) Volume, (b) total energy, (c) bandgap, (d) effective mass \(m^*/m_0\) of deformed SrTiO\(_3\). The inlet shows the deformation states, along the line A-A marked in (a) isotropic expansion, along B-B orthorhombic distortion with constant volume.
While pure SrTiO$_3$ is an insulator, doping with electron donating of SrTiO$_{2.875}$, which is the smallest concentration to be calculated by reduction and in the next section the influence of doping. In the case color of insulators into black. In this section we describe the oxygen requires sintering in oxygen reduced atmosphere turning the white lattice vacancies into black. In Fig. 3 of ref. 28, the donor band structure shows an additional donor band about 300meV below removing one oxygen atom in a 2x2x2 supercell, the electronic effective mass is almost the same as for pure SrTiO$_3$ ($m*_m0=4.9$), and at higher concentrations Sr$_{0.75}$TiO$_3$ even more $m*_m0>9$. Vacancies on the Ti-site increase the effective mass. In summary, any vacancies in small concentrations increase the effective mass.

![FIG. 4. Total density of states of deformed SrTiO$_3$: (a) isotropic expansion (line A-A in Fig. 3a), (b) orthorhombic distortion with constant volume (line B-B in Fig. 3a). The numbers refer to the lattice constants in pm.](image)

splitting smoothes the DOS distribution. In summary, the effective mass can be increased by a factor of 1.7 when the lattice is expanded by a factor of 1.1, but the expansion needs to be isotropic. These lattice constant expansion studies require less time-consuming calculations than the following studies of stochiometry deviations or doping, but are much more difficult in experiments.

**Lattice Vacancies**

While pure SrTiO$_3$ is an insulator, doping with electron donating ions like La$^{3+}$ for Sr$^{2+}$ or Nb$^{5+}$ for Ti$^{4+}$ turns SrTiO$_3$ into a $n$-type semiconductor. To maintain the charge balance the material needs to compensate the surplus charge by introducing oxygen vacancies, in other words, in order to obtain semi-conducting doped SrTiO$_3$, it requires sintering in oxygen reduced atmosphere turning the white color of insulators into black. In this section we describe the oxygen reduction and in the next section the influence of doping. In the case of SrTiO$_{2.875}$, which is the smallest concentration to be calculated by removing one oxygen atom in a 2x2x2 supercell, the electronic bandstructure shows an additional donor band about 300meV below the usual conduction band as shown in Fig. 10 c and in Fig. 3 of ref. 28. Concerning the curvature directly at $\Gamma$ in the $\Gamma$-$\Delta$ direction, the effective mass is almost the same as for pure SrTiO$_3$ ($m*_m0=4.4$), but compared to other bands it has less curvature in the $\Gamma$-$X$ or $\Gamma$-$R$ direction with a higher average effective mass ($m*_m0=1.8$) than pure SrTiO$_3$ (Table 2). Including the considerations of Fig. 1(b) about the non-parabolic behavior are taken into account, the mass is remarkably larger ($m*_m0>10$). However, when the oxygen content is lowered further (SrTiO$_{2.5}$, see Table 2), the additional band becomes strongly deformed and the mass decreases ($m*_m0<2$), as well as $m*_m0$. This result confirms that electronic effects strongly depend on the oxygen concentration range. Vacancies on the $A$- and $B$-sites were also studied. Low concentrations of vacancies on the Sr-site (Sr$_{0.875}$TiO$_3$) increases the effective mass slightly ($m*_m0=4.9$), and at higher concentrations Sr$_{0.75}$TiO$_3$ even more $m*_m0>9$. Vacancies on the Ti-site increase the effective mass. In summary, any vacancies in small concentrations increase the effective mass.

**Doping with La on A-site or Nb on B-site**

The doping concentrations necessary for turning SrTiO$_3$ into a $n$-type semiconductor in experiments are smaller than those achievable by present calculations ($x<0.12$), but the following results shows the trend. Substitution of Ti- by Nb-atoms in a 2x2x2 supercell as in SrTi$_{1-x}$Nb$_x$O$_3$ increases the effective band mass $m*$ steeply in both, the valence band ($m*_m0>20$, Fig. 5(d)) and conduction band ($m*_m0>8$, Fig. 5(c)). This increase in effective mass was confirmed also in 5x1x1 and 3x2x1 supercells for $x<0.25$. Above $x=0.25$, the effective mass suddenly drops to a low value of $m*_m0<3$. The DOS-mass, however, shows a smooth dependence on $x$ (Fig. 5(a)), while the bandgap decreases from 3.2 to about 2.5eV until $x=0.5$ and increase again (Fig. 6(a)). On the other hand, the doping on the B-site, Sr$_{1-y}$La$_y$TiO$_3$ shows a continuously increasing band gap (Fig. 6(b)) with $y$ and decreasing effective mass (Fig. 7), which will be explained later. The unusual increase of the effective band mass becomes clearer, when the details of the bandstructure of SrTi$_{1-x}$La$_x$O$_3$ with $x=0.12$ and 0.25, before and after the discontinuity in $m*$, are compared (Fig. 8). The double degenerated bands with large and small masses $m*_m0=4$ and 0.2 in SrTiO$_3$ split at the $\Gamma$ point in energy with a difference of 0.15eV. Between X-Z and X-R they is still degenerated, but becomes also suppressed at $x=0.12$ leading to the increase in $m*$. At $x=0.25$ (Fig. 5(b)) the energy degeneracy at $\Gamma$ between the bands with large and small masses vanishes and at $x=0.38$ also the degeneracy between X-Z and X-R is lost, although it reappears above $x \geq 0.75$. In the valence band a similar suppression of the degeneracy near $\Gamma$ occurs above 0.25, but above $x \geq 0.75$ the topology of bands is different than below $x < 0.25$, and causes the unsymmetrical behavior in Fig. 5(c) and (d). In summary, we can state that the large increase in effective mass is caused by degeneration in energy between a heavy and a light conduction band, both with lowest energy. This degeneration cannot be held at higher doping concentrations and the light band becomes lower in energy than the heavy one leading to a smaller bandgap and small $m_B$ between $x = 0.25$ and 0.75. In this concentration range the $m*$ relevant for macroscopic properties may become even smaller (0.2, as shown in Table 2) than shown as $m_C$ in Fig. 5(c), because the band with the light mass $m_C$ is now lower in energy (band with i=1) between $x=0.25$ and 0.75. This concentration range is distinguished from the usual case of a heavy conduction band at lowest energy, with the open symbols in Fig. 5(c).

Such behavior in the bandstructure occurs similarly for Sr$_{1-x}$La$_x$TiO$_3$, the La-doping on the A-site, namely the splitting of a degenerated SrTiO$_3$-band into a light band and a heavy band with increasing $y$. At the same concentration as in the Nb-case, $y=0.25$, the light band is shifted about 40meV below the heavy band, marked
with open symbols in Fig. 6, which shows the average effective mass \( m^* \). At the same time the effective band masses decreases to \( m_B/m_0 = 3.6 \), which leads to a smaller average effective mass than SrTiO\(_3\), \( m^* = 3.7 \) or 4.3 (Table 2, Fig. 6) for \( a = a_0 \) or \( a = 0.99a_0 \), respectively. This decrease in effective mass is smooth, different from the Nb-case and was also observed in the experiments\(^5\). The density-of-states envelope has almost the same shape for all concentrations (Fig. 6(b)), yielding a nearly constant \( m_{DOS} = 3.85 \). However, the bandgap increases with \( y \) from 3.2 to 4eV. In summary, La-doping decreases the effective mass almost linearly, while Nb-doping increases the mass steeply until the separation of the heavy and light bands causes a drastic decrease.

**FIG. 5.** Effective mass as a function of the Nb-composition \( x \) in SrTi\(_{1-x}\)Nb\(_x\)O\(_3\). (a,b) show the effective DOS-mass for the (a) conduction band, (b) valence band, (c,d) effective band mass \( m^* \) (bright line) and \( m_{B,h} \) (dark line) for (c) conduction band, and (d) valence band. The lines are eye guides. Filled and open symbols refer to heavy and light bands at lowest energy; rhombic, square and round symbols refer to 2x2x2, 5x1x1, and 3x2x1 supercell-calculations, respectively.

**FIG. 6.** Density of states for (a) Nb-doped, (b) La-doped SrTiO\(_3\)
SrTiO₃-related perovskites, the lattice constants change slightly but the order half- would need to be occupied by valence (+1)-elements (Table 3). These strong that in order to stabilize the perovskite structure, the substitutions of other elements on A- or B-site i=1, bright i=2). When other elements are substituted on the SrTi₀.₆Nb₀.₄O₃ thin-film specimen, all other data point fit the graph linear decrease with La-concentration from Fig. 6. Except the m*/m₀ as a dotted line. The bright line in Fig. 9 refers to the steep increase of effective mass with increasing lattice constant from Fig. 4(d) is shown. This calibration avoids the difficulties caused by impure samples and non-parabolic bands. The increase of the effective masses when passing through a defect. This can explain why a large effective mass is measured in the experiment SrTi₁ₓNbₓO₃₋ᵥ with x=0.02, while in simulation a combination of Nb-doping and oxygen vacancies leads to small effective masses (Table 2). The explanation is that the one-band approximation treated here is valid for nearly free electrons, as in pure SrTiO₃, where the CBM and VBM lie at the Γ-point. In heavily doped or oxygen deficit semiconductors the chemical potential is shifted, so that bands cross the Fermi level. In this case we determined the effective band masses m₁ₓ for band states close to the Fermi level. In order to verify the large effective mass in experiments, we treat both defects separately and use the 300meV Oxygen deficit band level (SrTiO₃₋ᵥ v=0.98) as donor state and the high effective mass maintain their large effective mass when passing through a defect.

**Table 3 Calculated effective mass of several SrTiO₃-related perovskite phases**

| Composition  | Lattice constants a₀ [nm] | Magnetic moment | Effective band mass m₁ₓ/m₀ at Γ-∆ | Effective mass m₁ₓ/m₀ |
|--------------|---------------------------|-----------------|-----------------------------------|-----------------------|
| A-site substituion |                          |                 |                                   |                       |
| CaTiO₃       | 0.3795                    | 0               | 4.0                               | 4.0                   |
| SrTiO₃       | 0.3905                    | 0               | 4.4                               | 4.8                   |
| BaTiO₃       | 0.4014                    | 0               | 4.8                               | 5.3                   |
| B-site substituion |                          |                 |                                   |                       |
| SrVO₃        | 0.3842                    | 0.13            | 8.0                               | 10.0                  |
| SrTiO₃       | 0.3905                    | 0               | 4.4                               | 4.8                   |
| SrMoO₃       | 0.3965                    | 0.01            | 4.0                               | 3.2                   |
| SrNbO₃       | 0.4112                    | 0               | 3.0                               | 2.7                   |
| SrZrO₃       | 0.4093                    | 0               | 2.0                               | 1.7                   |
| SrHfO₃       | 0.4114                    | 0               | 1.3                               | 1.1                   |
| SrMnO₃       | 0.3821                    | 3.0             | 0.3                               | 0.2                   |
| SrFeO₃       | 0.3851                    | 3.27            | 0.3                               | 0.1                   |
| SrCoO₃       | 0.3835                    | 2.28            | 0.3                               | 0.2                   |
| SrCuO₃       | 0.3810                    | 0               | 0.3                               | 0.1                   |

Defect Interaction: Doping and Oxygen vacancies

As described above, in order to keep the charge balance the n-doping in experiments is associated always with the formation of oxygen vacancies, but the vacancy concentration in experiments is much smaller than in simulation, otherwise the supercells for modeling are getting very large. Fig. 10 summarizes the main features of different simulated cases, a) no doping b) increased effective mass for x=0.12, c) 0.24, d) 0.37, which has been summarized in fig. 5d: leads to the steep increase of the effective mass until x=0.25, but at x>0.25 it leads to the break-through of a light band with very small mass m₁ₓ/m₀<0.2. When vacancies and lattice relaxation around them are introduced SrTi₁ₓNbₓO₃₋ᵥ (fig. 10 e, g) v=1.0, or f), b) v=0.24), a new band 300meV below the valence band minimum occurs, but the band curvature becomes complicated (fig 10 e-g). In order to explain the small doping concentration and large vacancy dilution in the experiment (x=0.02, and v=0.2) we suggest here that each defect can be treated as if separated. Hence, the bandstructure turns into quasi-p-n junctions as sketched in fig. 11b. The 300meV bands turn into donor levels below the Fermi-energy and traveling electrons maintain their large effective mass when passing through a defect. This can explain why a large effective mass is measured in the experiment SrTi₁ₓNbₓO₃₋ᵥ with x=0.02, while in simulation a combination of Nb-doping and oxygen vacancies leads to small effective masses (table 2). The explanation is that the one-band approximation treated here is valid for nearly free electrons, as in pure SrTiO₃, where the CBM and VBM lie at the Γ-point. In heavily doped or oxygen deficit semiconductors the chemical potential is shifted, so that bands cross the Fermi level. In order to verify the large effective mass in experiments, we treat both defects separately and use the 300meV Oxygen deficit band level (SrTiO₃₋ᵥ v=0.98) as donor state and the high effective mass m₁ₓ/m₀ > 12 of the Nb-doped case SrTi₁ₓNbₓO₃ x=0.02. This separation can explain the interaction of both defects with smaller concentration than calculations can perform.

**FIG. 7. Effective band mass m* for La-doped SrTiO₃.** (Dark symbols i=1, bright i=2).
Summarizing all results, four effects can be distinguished for doping with heavier elements in SrTiO₃, namely the enlargement of the atomic mass, the shift of the chemical potential, the enlargement of the lattice constants according to Vegards’ rule and Oxygen reduction due to the increase in the number of electrons. The enhanced calculated mass can be explained by the higher atomic mass in the order Ba, Sr and Ca, while for the B-site doping the shift in the chemical potential causes an opposite behavior. Additionally, in the case of most transition metals other than Ti on the B-site like V, Mn, Fe and Co, spin splitting occurs, which leads to a magnetic
### Discussion

The simulations on the SrTiO$_3$ and related single crystals showed a good agreement to experiments and show the validity of the effective mass concept, which is a simplified parameterization of the complex interaction between traveling electrons in the lattice. With Nb-doping the effective mass increases, whereas with La-doping it decreases. If we consider this as a general rule, it means that electron donation on the B-site leads to higher effective mass, while on the A-site it leads to smaller effective mass. Considering the substitution, the reverse behavior of A- and B-site is also obvious, as for substitutions of elements in the same row of the periodic system $A=Ca$, Sr, Ba $m^*/m_0$ increases; these were calculation results shown in table 3, and meanwhile experimentally verified. On the other hand, for $B=Ti$, Zr, Hf it decreases (table 3). In other words, in the case of electron injection by doping or a smaller orbital radius with heavier elements, both mechanisms lead obviously to the same result, with opposite effect for the A- or B-site. The increase in the effective mass in the case of BaTiO$_3$ leads to an increase in the Seebeck coefficient, which has indeed been found experimentally for Sr$_{0.9-z}$Ba$_z$La$_{0.1}$TiO$_3$ solid solutions. Although negligible at the considered temperatures, an increase in $m^*$ also leads to a reduction of the electronic part of the thermal conductivity, resulting in the maximum achievable dimensionless figure of merit $ZT=0.3$, $^{10, 42}$

We showed, that the preliminary discrepancy between the experimental effective mass of $m^*/m_0=7.2$ and the calculated one of $m^*/m_0=4.8$ almost disappears, because of several factors, namely, lattice expansion, oxygen deficit, doping and their interaction increases the effective mass. Other explanations for the increase in the effective mass caused by interactions with other electrons, atoms or the lattice, such as (a) relativistic effects in the vicinity of heavy atom cores, which might be responsible for the hump in the band-structure (Fig. 1), (b) an additional self-energy, (c) electron correlation effects, (d) charge density waves or (e) electron phonon coupling via polarons are some of the effects most commonly discussed in the literature. The investigations in this study showed that perovskite materials still have a potential for increased effective mass, which would further improve the Seebeck coefficient and other thermoelectric properties. This study focused on lattice strain and doping, and in a subsequent paper the effective mass of layered perovskites is reported.

### Summary

The thermoelectric power-factor can be improved, if the effective mass is increased, because the gain in Seebeck coefficient $S^2$ is larger than the decrease in the mobility. Using ab-initio calculations the effective mass of SrTiO$_3$ was calculated as $m^*/m_0=4.8$ which agrees well with experimental values. Lattice expansion increases the effective mass, but this increase is usually much less than that caused by electronic contributions due to doping or vacancies. Whether the
doping of electron donors occurs on the A- or B-site, it leads to opposite behavior concerning the effective mass, namely an increase for x for SrTi$_{1-x}$Nb$_x$O$_3$ and a decrease for Sr$_{1-y}$La$_y$TiO$_3$. The increase for Nb-doped SrTiO$_3$ can be explained by the flattening of the e$_{2g}$ band. With increasing doping concentration at x<0.25 the heavy and light bands at the Γ point split in energy, which leads to a dominance of the light electrons. For Sr$_{1-y}$La$_y$TiO$_3$ this splitting also occurs at y<0.25. Finally, the general finding of this study is that the effective mass $m_{DOS}$ derived from the density of states corresponds well to the average over effective masses of different electronic bands $m_{DOS}$, but the effective mass $m^*$ relevant for calculating the electrical conductivity requires detailed deduction from the bands close to the bandgap and the separation between doping and oxygen vacancies.

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References
1 S. Ohita, T. Nomura, H. Ohita, and K. Koumoto, J. Appl. Phys. 97 034106 (2005)
2. S. Ohita, T. Nomura, H. Ohita, and K. Koumoto, Appl. Phys. Lett. 87, 092108 (2005)
3. W. Wunderlich, Kunihito Koumoto, Internat. J. Materials Research 97 [5] 657-662 (2006)
4 Choongho Yu, Matthew L. Scullin, Mark Huijben, Ramamoorthy Ramesh, Arun Majumdar
Applied Physics Letters 92 092118 (2008)
5 H. Ohita, S-W. Kim, Y. Mune, T. Mizoguchi, Y. Ikuhara, M. Hirano, H. Hosono and K. Koumoto, Nature Materials 6 129 (2007)
6 Kyu Hyoung Lee, Yoriko Muna, Hiromichi Ohita, and Kunihito Koumoto,
Applied Physics Express 1 015007 (2008)
7 Wilfried Wunderlich, Hiromichi Ohita, and Kunihito Koumoto, Cond-mat/arXiv-0808.1772v1 (2008)
8 Y. Wang, K-H. Lee, H. Hyuga, H. Kita, K. Inaba, H. Ohita and K. Koumoto Appl. Phys. Lett. 91 242102 2007
9 Matthew L. Scullin, Choongho Yu, Mark Huijben, Sabroto Mukerjee, Jan Seidel, Qian Zhan, Joel Moore, Arun Majumdar, R. Ramesh, Applied Physics Letters 92 202113 (2008)
10 Masahiro Yamamoto Hiromichi Ohita and Kunihito Koumoto,
Appl. Phys. Lett. 90, 072101 (2007)
11 H. P. R. Frederikse, W. R. Thurber, and W. R. Hosler, Phys. Rev. 134, A442 (1964).
12 M. Ahrens, R. Merkle, B. Rahmati and J. Maier Physica B: Condensed Matter, 393 [1-2] (2007) 239-248
13 R. Moos, A. Gmudi, and K.H. Haertl, J.Appl.Phys.78 [8] 5042 (1995)
14 M. Marques, L. K. Teles, V. Anjos, L. M. R. Scolfaro, J. R. Leite, V. N. Freire, G. A. Farias, and E. F. da Silva, Appl.Phys.Lett. 82 [18] 3074 (2003)
15 T. Okuda, K. Nakanishi, S. Miyasaka, and Y. Tokura, Phys. Rev B 63 113104 (2001)
16 P. Calvani, M. Capizzi, F. Donato, S. Lupi, P. Maselli, and D. Peschiaroli, Phys. Rev. B 47, 8917 (1993)
17 H. Makino, I. H. Inoue, M. J. Rozenberg, I. Hase, Y. Aiura, and S. Onari, Phys. Rev. B 58, 4384 (1998)
18 D. L. Young, and T. J. Coutts, Rev. Sci. Instr. 71 [2] (2000) 462-466
19 W.K. Metzger, M.W. Wanlass, L.M. Gedvilas, J.C. Verley, J.J. Carapellar, and R.K. Ahrenkel, J.Appl.Phys. 92 [7] 3524 (2002)
20 C. B.Vining, J. Appl. Phys. 69 331 (1991)
21 G. Kresse, and J. Hafner, Phys. Rev. B 4914251 (1994).
22 P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, an Augmented Plane Wave 1 Local Orbitals Program for Calculating Crystal Properties (Karleheinz Schwarz, Techn. Universität Wien, Austria, 2001), ISBN 3-9501031-1-2.
23 W. Koshinae, K. Tsatsui, and S. Maekawa, Phys Rev B 62 11 6869 (2000)
24 M. Suzuki, T. Uenoyma, and A.Yanase, Phys.Rev. B 52 [11] 8132 (1995)
25 A. H. Kahn and A. J. Leyendecker, Phys. Rev. 135, A1321 (1964)
26 G. Fabricius, E. L. Peltzer y Blanca, C. O. Rodriguez, A. P. Ayala, P. de la Presa, and A. L. Garcia, Phys. Rev. B 55, 164 (1997)
27 S. Kohiki, M. Arai, H. Yoshikawa, S. Fukushima, M. Oku, and Y. Waseda, Phys. Rev. B 62, 7964 (2000)
28 W. Luo, W. Duan, S.G. Louie, and M.L. Cohen, Phys. Rev. B 70, 214109 (2004)
29 J. P. Buban, H. Iddir, and S. Ögüt, Phys. Rev. B 69, 180102 (2004)
30 N. Shanthi and D. D. Sarma, Phys. Rev. B 57, 21513 (1998)
31 T. Tanaka, K. Matsunaga, Y. Ikuhara, and T. Yamamoto, Phys. Rev. B 68, 205213 (2003)
32 Do Duc Cuong, Bora Lee, Kyeong Mi Choi, Hyo-Shin Ahn, Seungwu Han, and Jaichan Lee
Physical Review Letters 98 115503 (2007)
33 K. Kunagai, T. Suzuki, Y. Taguchi, Y. Okada, Y. Fujishima, and Y. Tokura, Phys. Rev. B 48, 7636 (1993)
34 M.Imada, A.Fujimori, and Y.Tokura, Rev.Mod.Phys. 70 [4] 1039 (1998)
35 K. Uchida, S. Tsuneyaki, and T. Shimizu, Phys. Rev. B 68, 174107 (2003)
36 K. Morito, T. Suzuki, S. Sekiguchi, H. Okushi, and M. Fujimoto, Jpn. J. Appl. Phys. 39166 (2000)
37 R. Kirchheim, Acta Materialia 55 5129 (2007)
38 S.A.Turzhevsky, D.L. Novikov, V.A.Gubanov, and A.J. Freeman, Phys.Rev.B 50 [5] 3200 (1994)
39 S.A. Howard, J.K.Kau, and H.U.Anderson, J. Appl. Phys 65 1492 (1994)
40 S. Lenjer, O. F. Schirmer, and H. Hesse, Phys. Rev. B 70, 157102 (2004)
41 Makoto Sakata “Thermoelectric Energy Conversion”, Shokabu Solids”, Cambride Unversity press (1972)
42 W. Muta, K. Kurosaki, and S.Yamanaka, J. Alloy. Comp. 368 22 (1995)
43 M. Suzuki, T. Uenoyama, and A.Yanase, Phys.Rev. B 52 [11] 8132 (1995)
44 W.K. Metzger, M.W. Wanlass, L.M. Gedvilas, J.C. Verley, J.J. Carapellar, and R.K. Ahrenkel, J.Appl.Phys. 92 [7] 3524 (2002)
45 C. B.Vining, J. Appl. Phys. 69 331 (1991)