First-principles Modelling of SrTiO₃ based Oxides for Thermoelectric Applications

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Using first-principles electronic structure calculations, we studied the electronic and thermoelectric properties of SrTiO₃ based oxide materials and their nanostructures identifying those nanostructures which possess highly anisotropic electronic bands. We showed recently that highly anisotropic flat-and-dispersive bands can maximize the thermoelectric power factor, and at the same time they can produce low dimensional electronic transport in bulk semiconductors. Although most of the considered nanostructures show such highly anisotropic bands, their predicted thermoelectric performance is not improved over that of SrTiO₃. Besides highly anisotropic character, we emphasize the importance of the large weights of electronic states participating in transport and the small effective mass of charge carriers along the transport direction. These requirements may be better achieved in binary transition metal oxides than in ABO₃ perovskite oxide materials.

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I. INTRODUCTION

Thermoelectric (TE) technology exploits the ability of certain materials for direct and reversible conversion of thermal energy into electricity. This double edge ability gives TE technology a strong appeal in almost all energy-related applications. Nevertheless, many fundamental problems have to be solved and in particular the intrinsic efficiency of TE materials still needs to be significantly improved before TE technology becomes a competitive alternative. The efficiency of a TE material depends on the dimensionless figure of merit, $ZT = \sigma S^2 T/\kappa T$, where $\sigma$ is the electrical conductivity, $S$ is the thermopower or Seebeck coefficient, $T$ is the absolute temperature, $\kappa_T$ is the total thermal conductivity including electronic and lattice contributions, and $S^2/\sigma$ is the power factor (PF). Improving TE efficiency is not obvious because the parameters entering $ZT$ are interlinked, and cannot be optimized independently. Moreover, $ZT$ has to be optimized in a $T$ range at which the TE devices will operate. Many interesting TE applications function at high $T$, and for practical applications other aspects are also very important such as: the cost of materials, their stability at high $T$, their toxicity, and availability.

Oxide materials are not known to exhibit the highest TE performance, but they offer stability in oxidizing and corrosive environments at high $T$ (T>800 - 1000 K). In this context, oxides appear very appealing for high $T$ applications. Consequently, efforts have been devoted over the last 15 years to the optimization of TE properties of both n-type and p-type oxide materials. Good candidates for n-type materials include Nb-, W-, La-, Ce-, Pr-, Nd-, Sm-, Gd-, Dy-, and Y-doped SrTiO₃, Nb-, La-, Nd-, Sm-, and Gd-doped Sr₂TiO₄, and Sr₂Ti₂O₇, La-doped CaMnO₃ or Al-, Ge-, Ni- and Co-doped ZnO, Er-doped CdO, TiO₂, Nb₂O₅, WO₃, while for p-type materials the most promising compounds are Ca₃Co₄O₉ with $ZT \sim 0.3$ at 1000 K, and BiCuSeO with $ZT \sim 1.4$ at 923 K. Many studies have concerned doped SrTiO₃, demonstrating the largest $ZT \sim 0.4$ in SrTiO₃:Nb₂O₃ films at 1000 K, and $ZT \sim 0.41$ in bulk Sr₁₋₃x/LaₙTiO₃ at 973 K. Different strategies have been proposed to further increase TE efficiency. Attempts to decrease the lattice thermal conductivity $\kappa_l$ by atomic substitution of Sr by Ba have been envisaged but seem to negatively affect the TE performance. A more promising approach is the reduction of $\kappa_l$ from scattering of phonons at interfaces, highlighted in layered Ruddlesden-Popper (RP) compounds. Also, Ohta al. demonstrated significant enhancement of $S$ arising from electron confinement and the formation of two dimensional electron gas (2-DEG) in SrTiO₃/Nb-SrTiO₃ superlattices. Although very promising, the inactive SrTiO₃ interlayer must be sufficiently large to avoid electron tunneling and to get significant enhancement of $S$. This decreases the effective TE performance. In order to maximize TE performance, we showed that the 2-DEG has to be achieved in doped semiconducting nanostructures rather than those with metallic character. Few first-principles studies have investigated the electronic properties of Nb-doped SrTiO₃ and Zr₂TiO₄ and a few studies have addressed TE properties of SrTiO₃, BaTiO₃, PbTiO₃, CaTiO₃, KTaO₃, HoMnO₃, CaMnO₃, Ca₃Co₄O₉, ZnO, Cu₂O, CdO, TiO₂, and V₂O₅. At this stage, a complete understanding of the transport properties and moreover of the band structure engineering in oxide materials is still missing.

Employing the concept of electronic band structure engineering and our guidance ideas, we showed recently that very anisotropic flat-and-dispersive electronic bands...
are able to maximize the $PF$ and carrier concentration $n$ of bulk semiconductors, and at the same time to produce low-dimensional electronic transport (low-DET). In practice this is typically achieved from the highly directional character of some orbitals like the $d$ states. Transition metal (TM) oxides with $d$-type conduction states appear as a well suited playground to explore this concept. Also the rich chemical crystalinity of oxides encourages strategies of multiscale nanostructuring by considering hybrid crystal structures that contain discrete structural blocks or layers. The nanostructuring of such hybrid materials is possible in order to engineer their electronic band structures and to lower their $\kappa_t$. Therefore, in this theoretical work, we studied TE properties of SrTiO$_3$ based materials and their nanostructures. We have considered the (SrTiO$_3$)$_m$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_m$-(KnbO$_3$)$_1$ superlattices (SL). LaVO$_3$ is a Mott insulator with an electronic band gap $E_g \sim 1.1$ eV [65], which shows a $PF \sim 0.06$ mW/mK$^2$ at 1000 K. [66] For (SrTiO$_3$)$_m$-LaVO$_3$ nanostructures we expect an electronic transport achieved through LaVO$_3$ layers since it has a smaller band gap that SrTiO$_3$ ($E_g \sim 3.3$ eV), which may give rise to low-DET and enhanced $PF$. We consider (SrTiO$_3$)$_m$-KnbO$_3$ SL in order to compare their results with those of Nb-doped SrTiO$_3$. We also studied TE properties of Sr and Co based naturally-ordered Ruddlesden-Popper compounds (AO[ABO$_3$]$_m$), which are more easy to control experimentally and more realistic for practical applications than artificial nanostructures.

II. TECHNICAL DETAILS

The structural, electronic and TE properties of considered oxide structures were studied within density functional theory (DFT) formalism using the hybrid functional B1-WC. B1-WC hybrid functional describes the electronic properties (band gaps) and the structural properties with a better accuracy than the usual simple functionals, being more appropriate for correlated materials such as oxides. [67] [68] For comparison of bulk SrTiO$_3$ results, we also used approximations based on LDA [70], GGA(PBE [71] and GGA-WC [72]) usual simple functionals. The electronic structure calculations have been performed using the linear combination of atomic orbitals method as implemented in CRYSTAL first-principles code. [73] We used localized Gaussian-type basis sets including polarization orbitals and considered all the electrons for Ti [74], O [75], V [77], K and Nb [76], F and Co [77]. The Hartree-Fock pseudopotential for Sr [75], and the Stuttgart energy-consistent pseudopotential for La [79] were used.

In order to go beyond the rigid band approximation, we considered $3 \times 3 \times 3$ SrTiO$_3$ perovskite supercells with $PT$ symmetry, which incorporate explicitly two Nb and two La doping elements per supercell. For (SrTiO$_3$)$_m$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_m$-(KnbO$_3$)$_1$ nanostructures, we have considered $a \times a \times c$ SL with $P4mm$ symmetry to treat the nonmagnetic and ferromagnetic (FM) order, and $\sqrt{2}a \times \sqrt{2}a \times c$ SL with $P4bm$ symmetry for the FM and antiferromagnetic (AFM) orders, where $a$ is the lattice constant of cubic perovskite structure. For AO[ABO$_3$]$_m$ SL with $I4/mmm$ symmetry the body centered primitive cells were used in calculations. According to the position of F at the apical site, the symmetry of Sr$_2$Co$_3$F$_7$ has been reduced to $Cmcm$ and $Cmmm$ space groups for type I and type II ordered structures, respectively. For these F ordered structures, we used the face centered primitive cells in our calculations.

Brillouin zone integrations were performed using the following meshes of $k$-points: $6 \times 6 \times 6$ for bulk SrTiO$_3$, Sr$_2$TiO$_4$, and Sr$_2$CoO$_4$F, $3 \times 3 \times 3$ for La and Nb doped $3 \times 3 \times 3$ SrTiO$_3$ supercells, $6 \times 6 \times 4$ for (SrTiO$_3$)$_1$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_1$-(KnbO$_3$)$_1$ SL, $6 \times 6 \times 1$ for (SrTiO$_3$)$_2$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_2$-(KnbO$_3$)$_1$ SL, and $4 \times 4 \times 4$ for Sr$_3$Ti$_2$O$_7$. The self-consistent-field calculations were considered to be converged when the energy changes between interactions were smaller than $10^{-8}$ Hartree. An extra-large predefined pruned grid consisting of 75 radial points and 974 angular points was used for the numerical integration of charge density. Full optimizations of the lattice constants and atomic positions have been performed with the optimization convergence of $5 \times 10^{-5}$ Hartree/Bohr in the root-mean square values of forces and $1.2 \times 10^{-3}$ Bohr in the root-mean square values of atomic displacements. The level of accuracy in evaluating the Coulomb and exchange series is controlled by five parameters. [73] The values used in our calculations are 7, 7, 7, 7, and 14.

The transport coefficients were estimated in the Boltzmann transport formalism and the constant relaxation time approximation using BoltzTraP transport code. [80] The electronic band structures (energies), used in the transport calculations, were calculated with electronic charge densities converged for denser $k$-point meshes (doubling the $k$-point meshes in optimization calculations). The transport coefficients were very well converged for the energies calculated on $k$-point meshes of $59 \times 59 \times 59$ for bulk SrTiO$_3$, Sr$_2$TiO$_4$, Sr$_2$Ti$_2$O$_7$, and Sr$_2$CoO$_4$F, $27 \times 27 \times 27$ for La doped $3 \times 3 \times 3$ SrTiO$_3$ supercell, $59 \times 59 \times 41$ for (SrTiO$_3$)$_1$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_1$-(KnbO$_3$)$_1$ SL, and $59 \times 59 \times 23$ for (SrTiO$_3$)$_2$-(LaVO$_3$)$_1$ and (SrTiO$_3$)$_2$-(KnbO$_3$)$_1$ SL.

The effective masses were obtained by calculating values of energy close to conduction band (CB) minimum and valence band (VB) maximum while moving from the extremum points along the three directions of the orthogonal reciprocal lattice vectors $k_i$ ($i=x, y, z$). The energy values, $\epsilon_k$, were fitted up to 10-th order polynomials in $k_i$. In general $\epsilon_k$ can be expanded about an extremum point as:

$$
\frac{2m_e}{\hbar^2} \epsilon_k = \sum_{i,j} \frac{m_{ij}}{m_{ij}} k_i k_j
$$

where $m_{ij}$ are the components of the effective mass tensor.
TABLE I: Lattice constant \( a \), and indirect band gap \( E_g \) of SrTiO\(_3\) perovskite structure estimated within different functionals. The experimental values are included for comparison.

| Functional | LDA | PBE | GGA-WC | B1-WC | Exp. |
|------------|-----|-----|--------|-------|------|
| \( a(\text{Å}) \) | 3.864 | 3.943 | 3.898 | 3.880 | 3.890\textsuperscript{a} |
| \( E_g(\text{eV}) \) | 2.24 | 2.25 | 2.25 | 3.57 | 3.25\textsuperscript{b} |

\textsuperscript{a}Extrapolated at 0 K from Ref. [82].
\textsuperscript{b}From Ref. [83].

The oxide compounds under study are well known to exhibit various types of structural phase transitions with temperature. Since we are interested in TE at high T, in first approximation we restricted our investigation to the high symmetry phases of \( Pm\bar{3}m \) for bulk perovskites and \( P4mm, P4bm \), and \( I4/mmm \) for superlattices. Some of them are also expected to show magnetic order at high T and be in a paramagnetic configuration at high T. For the later we compare different magnetic orders to find the systems with lower total energy and more structurally stable.

### III. RESULTS

FIG. 1: (Color online) Electrical conductivity \( \sigma \), Seebeck coefficient \( S \), and power factor \( PF = S^2/\sigma \) dependence on chemical potential for SrTiO\(_3\) estimated at 300 K within B1-WC using the relaxation time \( \tau = 0.43 \times 10^{-14} \) s. The n-type doping carrier concentration \( n = 1 \times 10^{21} \text{ cm}^{-3} \) is shown in dashed vertical line.

A. Bulk SrTiO\(_3\) and its alloys

The structural (lattice constant) and electronic (band gap) properties of bulk SrTiO\(_3\) optimized within the different functionals are given in Table I. LDA underestimates the lattice constant and the atomic volume, whereas PBE overestimates these properties, which is the typical behaviour of LDA and PBE functionals. GGA-WC describes very well the structural properties of SrTiO\(_3\), being a functional developed for solids. All the simple functionals underestimate SrTiO\(_3\) band gap, which is an inherent problem of DFT. B1-WC hybrid, which mixes the GGA-WC with a small percentage of exact exchange (16%) describes simultaneously both the structural and electronic properties with good accuracy.

For a more complete theoretical characterization, we have studied also TE properties (\( \sigma, S, \) and \( PF \)) of bulk SrTiO\(_3\) within B1-WC hybrid, and the other used simple functionals. In the constant relaxation time approximation, the relaxation time \( \tau \) is considered as a constant \( \tau = \tau_0 \) independent of energy and temperature \( T \), and is estimated from fitting of the experimental electrical conductivity \( \sigma_{exp} \) at a given doping carrier concentration \( n \) and \( T \). \( \tau \) within the different functionals was estimated by fitting the room temperature experimental values \( \sigma_{exp} = 1.4 \times 10^5 \text{ S/m at } n = 8 \times 10^{20} \text{ cm}^{-3} \) [81], and \( \sigma_{exp} = 1.667 \times 10^5 \text{ S/m at } n = 1 \times 10^{21} \text{ cm}^{-3} \) [82] (Table II). The resulting value of \( \tau \) is \( \sim 0.43 \times 10^{-14} \) s, which is very similar in all the used functionals (see Table II). The estimated values of \( \sigma, S, \) and \( PF \) at 300 K as a function of chemical potential within B1-WC hybrid are given in Fig. 1. For n-type doping, \( PF \) is \( \sim 1 \text{ mW/mK}^2 \), being underestimated with respect to experiment \( \langle PF_{exp} \rangle \sim 3 \text{ mW/mK}^2 \) [82, 83]. This underestimation of \( PF \) is due to a low value of thermopower \( S \sim -77 \mu\text{V/K} \) in comparison with the experimental value of \( S_{exp} \sim -147 \mu\text{V/K} \) at \( n = 1 \times 10^{21} \text{ cm}^{-3} \) and 300 K. \( PF \) estimated within the usual simple functionals (LDA, GGA-WC) has the same value \( \sim 1 \text{ mW/mK}^2 \) (Fig. 2).

The promising TE properties of SrTiO\(_3\) based oxides were found for strong n-type doping \( (n \sim 10^{21} \text{ cm}^{-3}) \), carrier concentrations which are more than one order of magnitude higher than those of typical TE materials such as PbTe, Bi\(_2\)Te\(_3\)). At these high concentrations, the underestimation of \( PF \) within all considered functionals may be generated by the incomplete validity of rigid band structure approximation (Fig. 2). In order to check this, we have considered \( 3 \times 3 \times 3 \) SrTiO\(_3\) supercells which explicitly incorporate La and Nb doping elements, and
studied their structural, electronic and transport properties. These doping elements introduce one electron to the systems, and change also the electronic states close to the Fermi level generated by doping. Results suggest that PF slightly larger than those of bulk SrTiO$_3$. The Fermi energy $E_F$ is shown in red dashed line. DOS of bulk SrTiO$_3$ is shown in background brown color.

We assign the underestimation of $PF$ for $3\times3$ SrTiO$_3$ supercells, estimated at 300 K within B1-WC, are also shown.

We studied TE properties of $3\times3$ SrTiO$_3$ supercells, which include explicitly La doping elements ($3\times3$ La: SrTiO$_3$). The relaxation time determined by fitting $\sigma_{exp}$ at $n = 1 \times 10^{21}$ cm$^{-3}$ and 300 K is the same as that of bulk SrTiO$_3$ ($\tau = 0.45 \times 10^{-14}$ s). Although the electronic states near the Fermi level of $3\times3$ La: SrTiO$_3$ supercell are slightly different than those of bulk SrTiO$_3$ at high values of $n = 1.2 \times 10^{21}$ cm$^{-3}$ (Fig. 3(b)), $PF$ is comparable with that of bulk SrTiO$_3$ (Fig. 2). Therefore, the underestimation of experimental power factors $PF_{exp}$ of $\sim2$-3 mW/mK$^2$ is not due to the change of electronic states close to Fermi level generated by doping. Kinaci et al. also showed that La, Nb and Ta doping do not change significantly the electronic states close to the Fermi level, and TE properties of SrTiO$_3$ alloys are comparable with those of bulk SrTiO$_3$. [$S5$] $S$ values for SrTiO$_3$ alloys are slightly lower, whereas $\sigma$ values are slightly larger than those of bulk SrTiO$_3$. [$S5$] These results suggest that $PF$ of SrTiO$_3$ alloys is not expected to increase significantly with respect to that of bulk SrTiO$_3$.

We assign the underestimation of $PF_{exp}$ to the enhancement of carrier effective mass due to the electron-phonon coupling interaction, which is compatible with the fact that the electronic transport in n-type SrTiO$_3$ has a polaronic nature. [$S5$] A factor of 3 larger inertial effective mass $m_i^*$ was obtained from experimental optical conductivity relative to the theoretical $m_i^*$ value of $\sim0.63m_e$ estimated within LDA. [$S5$] At a given carrier concentration, larger experimental effective masses generate larger $S_{exp}$ by lowering the chemical potential relative to CB bottom. We have estimated $m_i^*$ according to the relation [80]:

$$\frac{1}{m_i^*} = \frac{1}{3} \left( \frac{2}{m_l} + \frac{1}{m_h} \right)$$

where $m_l$ and $m_h$ are the light and heavy effective masses.
of the three fold degenerate \( t_{2g} \) bands which form the CB bottom. The estimated \( m_t \), \( m_h \), and \( m_i^* \) values are within B1-WC(LDA), respectively. Since in the transport calculations we do not account for the polaronic nature of SrTiO\(_3\) conductivity, this translate into small values of the estimated relaxation time (see Table I).

**B. Band structure engineering in SrTiO\(_3\) based nanostructures**

We considered \((\text{SrTiO}_3)_m(\text{NbO}_3)_1\) and \((\text{SrTiO}_3)_m(\text{LaVO}_3)_1\) SL nanostructures with \( m=1, 5 \) for which we studied the electronic and transport properties, and described the relation between size of nanostructures and their TE properties by looking at the effect of quantum confinement on PF. \((\text{SrTiO}_3)_{5}(\text{NbO}_3)_1\) SL with \( m=1, 5 \) have a nonmagnetic ground state. Their structures and electronic band structures are shown in Figs. 4(a),(b), and 5(a),(b). In comparison to bulk SrTiO\(_3\), \((\text{SrTiO}_3)_1(\text{NbO}_3)_1\) SL possess smaller \( E_g \), and an electronic band which is very flat along \( \Gamma Z \) direction and dispersive in the other orthogonal directions of the Brillouin zone (see Fig. 6(b)). This very flat-and-dispersive band forms the CB bottom and has a Nb \( d_{xy} \) orbital character. The electronic states associated to this very anisotropic band, which participate in the electronic transport, have a reduced weight (short \( \Gamma Z \) distance in the Brillouin zone). The weight is proportional with the density of states DOS and the carrier pocket volumes inside of the Brillouin zone. The reduced weight can be seen more easily from DOS scaled to ABO\(_3\) formula unit (f.u.) (see Fig. 7(a)). The electronic states inside of SrTiO\(_3\) band gap have a small weight, which generate in the inplane direction power factors \( PF_{xx} \) smaller than that of bulk SrTiO\(_3\) (Fig. 8(a)). In the cross plane direction, \((\text{SrTiO}_3)_1(\text{NbO}_3)_1\) SL show large power factors \( PF_{zz} \) but at very high \( n \) values (chemical potential \( \mu \sim 2.75 \) eV) which can not be achieved in experiment. Increasing the quantum confinement in the case of \((\text{SrTiO}_3)_5(\text{NbO}_3)_1\) SL, decreases the weight of very anisotropic flat-and-dispersive Nb \( d \) band. The decrease in weight of this anisotropic band can be seen from the electronic band structure and DOS (see Figs. 5(b), 7(a)), and produces a PF drop relative to \((\text{SrTiO}_3)_1(\text{NbO}_3)_1\) SL (Fig. 8(a)).

SL formed by \((\text{SrTiO}_3)_m(\text{LaVO}_3)_1\) with \( m=1, 5 \) have an antiferromagnetic (AFM) ground state. Their structures and electronic band structures are shown in Figs. 4(c),(d), and 5(c),(d). These SL possess two electronic bands laying inside of SrTiO\(_3\) band gap, which are very flat in \( \Gamma A \) and \( AZ \) directions, and weakly dispersive in the other directions of Brillouin zone (Fig. 6(b)).

**FIG. 5:** Electronic band structure of: (a) \((\text{SrTiO}_3)_1(\text{KnBo}_3)_1\), (b) \((\text{SrTiO}_3)_5(\text{KnBo}_3)_1\), (c) \((\text{SrTiO}_3)_1(\text{LaVo}_3)_1\), (d) \((\text{SrTiO}_3)_5(\text{LaVo}_3)_1\), and (e) bulk SrTiO\(_3\) estimated within B1-WC.

**FIG. 6:** (Color online) Brillouin zone of: (a) simple cubic \( \text{SrTiO}_3\), (b) tetragonal \((\text{SrTiO}_3)_1(\text{KnBo}_3)_1\) and \((\text{SrTiO}_3)_5(\text{LaVo}_3)_1\) SL \((m=1,5)\), (c) body centered tetragonal \( \text{SrO}[\text{SrTiO}_3]_1\) \((m=1,2)\), and (d) one face centered tetragonal \( \text{Sr}_2\text{CO}_2\text{F}\) (ground state structure from Fig. 2(c)). The high symmetry points along the directions used in electronic band structures, and the orthogonal reciprocal \( k_i \) vectors \((i=x,y,z)\) are also shown.
These flat bands create a narrow energy distribution with a very large weight on the top of valence band, being generated by V $d_{xz}$ and $d_{yz}$ orbitals. The very large weight of this narrow energy distribution can be seen from DOS, and this distribution generates PFs smaller than those of SrTiO$_3$ (see Figs. 7(b), and 8(b)). This shows that a single or multiple very flat bands having large effective masses in all directions of Brillouin zone are not able to enhance TE performance, since the charge carriers associated to such flat bands are very localized and unable to participate in electronic transport. Increasing the quantum confinement in (SrTiO$_3$)$_3$(LaVO$_3$)$_1$ SL, also lowers the weight of narrow energy distribution and PF of these SL (see Figs. 7(b), and 8(b)).

C. Band structure engineering in AO[ABO$_3$]$_m$ naturally-ordered Ruddlesden-Popper phases

Highly anisotropic flat-and-dispersive bands can be found also in AO[ABO$_3$]$_m$ Ruddlesden-Popper naturally-ordered compounds. These compounds are formed from ABO$_3$ perovskite layers separated by an AO atomic layer and can nowadays be grown epitaxially with atomic-scale control.[87] To search for highly anisotropic bands, we have considered SrO[SrTiO$_3$]$_m$ (m=1 and 2) and SrO[SrCoO$_2$F]$_1$ compounds (Fig. 7). The insertion of SrO atomic layer in the crystallographic direction $Oz$ creates the quantum confinement of electronic states in $\Gamma Z$ direction from the band structure of Sr$_2$TiO$_4$ and Sr$_3$Ti$_2$O$_7$ (see Fig. 10(a),(b)). It can be seen that CB bottom is formed by such very anisotropic bands, which generate narrow energy distributions with small weights (small length of $\Gamma Z$ direction). The small weights of these distributions close to CB minimum (energy $\sim$1.75 - 2 eV) can be seen more easily from scaled DOS per f.u. of
Sr$_2$TiO$_4$ and Sr$_3$Ti$_2$O$_7$, (Fig. 11(a)).

TE properties have been estimated using the same value of $\tau$ as that of bulk SrTiO$_3$, because we want to compare the electronic contribution given by the electronic band structure of these naturally-ordered compounds to that of bulk SrTiO$_3$. Due to the small weight of narrow energy distribution, the n-type PF corresponding to the chemical potential $\sim 1.75 - 2$ eV in Ox direction ($PF_{xx}$) is smaller than that of bulk SrTiO$_3$ (Fig. 12(a)). In the approximation that $\tau$ of SrO[SrTiO$_3$]$_m$ compounds is similar to that of bulk SrTiO$_3$, the n-type PFs is not improved.

From Co based AO[ABO$_3$]$_m$ compounds, we have explored the cobalt oxyfluoride Sr$_2$CoO$_3$F, in which F substitute O form apical position of CoO$_6$ octahedron. In Figure 9(c-f) are shown the model structures in which F substitute one O atom (Fig. 9(c),(d)) or two O atoms (Fig. 9(e),(f)) form apical positions and Co atoms have AFM/FM order. The analysis of structural properties shows that the ground state structure is the structure in which F substitute one O atom form apical positions and Co atoms have AFM order (Fig. 9(c)). These results are in agreement with the experimental study, which finds G-type antiferromagnetic order of Co in Sr$_2$CoO$_3$F. For the ground state structure, we studied the electronic and transport properties. The electronic band structure of Sr$_2$CoO$_3$F contains two electronic bands with Co $d$ orbital character in the (0.75eV, 1.25eV) energy interval (Fig. 10(c)). These bands do not have a very anisotropic character, requirement identified to maximize PF. As a result the energy distribution of the two Co bands is narrow and has large weight, which can be seen from DOS (Fig. 11(b)). In the approximation that $\tau$ of Sr$_2$CoO$_3$F is comparable to that of Sr$'$(TiO$_3$, the transport calculations show that PF of these compounds is smaller than that of Sr$'$(TiO$_3$ (Fig. 12(b))

D. Comparison of the different nanostructures with bulk SrTiO$_3$

In the approximation that $\tau$ of the considered nanostructures is comparable to that of bulk SrTiO$_3$, none of the nanostructures shows higher TE performance than bulk SrTiO$_3$, in spite of the fact that some of them possess highly anisotropic flat-and-dispersive TM $d$ ele-

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**FIG. 10:** Electronic band structure of: (a) Sr$_2$TiO$_4$, (b) Sr$_3$Ti$_2$O$_7$, (c) Sr$_2$CoO$_3$F (ground state structure from Fig. 9(c)), and (d) bulk SrTiO$_3$ estimated within B1-WC.

**FIG. 11:** (Color online) Total density of states (DOS) of: (a) Sr$_2$TiO$_4$ and Sr$_3$Ti$_2$O$_7$, and (b) Sr$_2$CoO$_3$F (ground state structure from Fig. 9(c)) scaled to formula unit (f.u.= Sr$_2$TiO$_4$, Sr$_{1.5}$TiO$_{3.5}$, and Sr$_2$CoO$_3$F, respectively).
tronic bands. In addition, the electronic states associated to these bands which participate in transport must have significant weights in order to maximize $PF$ and $n$. The weights are proportional to DOS which depends on the density of states effective mass $m_d^* = \gamma^{2/3}(m_h^2m_l^2)^{1/3}$, where $\gamma$ is the carrier pocket degeneracy or band multiplicity.\footnote{From Ref. [62].} Therefore in Table II we show the estimated values of DOS($\mu$)/f.u. at the chemical potential $\mu$ which optimizes n- and p-type $PF$s, $m_d^*$, and band anisotropy ratio $R = m_h/m_l$. The usual anisotropic behavior is for heavy masses $m_h$ across SL direction ($Oz$), and light masses $m_l$ in the inplane SL direction ($Ox$, $Oy$). Although (SrTiO$_3$)$_1$(K NbO$_3$)$_1$ SL show very large $R$ and large $m_d^*$ values, their DOS($\mu$)/f.u. corresponding to the maximum n-type $PF$ is about one order of magnitude smaller than that of SrTiO$_3$. The confinement of Nb $d_{xy}$ states achieved in these SL is able to create very large anisotropic electronic bands, but with small weights of the electronic states participating in transport due to their small carrier pocket volume in the Brillouin zone. (SrTiO$_3$)$_1$(LaVO$_3$)$_1$ SL at Z point of VB maximum, show unusual band anisotropic behavior with $m_l$ along $z$ direction and $m_h$ along $x$ and $y$ directions, which gives large values for $R$, $m_d^*$, DOS($\mu$)/f.u. at the p-type $PF$ maximum, and larger p-type power factor across SL direction ($PF_{xx}$) than along SL direction ($PF_{zz}$). Similar to (SrTiO$_3$)$_1$(K NbO$_3$)$_1$ SL, the confinement of Ti $t_{2g}$ ($d_{xy}$) states participating in transport of Sr$_2$TiO$_4$ and Sr$_3$Ti$_2$O$_7$ naturally-ordered SL creates large anisotropy ratios, but at the same time detrimental reduced weights. On the other hand, Co $t_{2g}$ ($d_{xz}$, and $d_{yz}$) states involved in the n-type transport of Sr$_2$CoO$_4$F have large weights, but small anisotropy ratio. For comparison, we show in Table II the corresponding values for the full Heusler Fe$_2$TiSi which shows very large n-type $PF$s.\footnote{From Ref. [62].} These very large $PF$s are achieved for concomitant large anisotropy ratio and weights, and small $m_l$ effective mass which gives large carrier mobilities along the transport direction.

**IV. CONCLUSIONS**

Using the concept of electronic band structure engineering we tried to design materials possessing highly anisotropic electronic bands in (SrTiO$_3$)$_m$(K NbO$_3$)$_1$ and (SrTiO$_3$)$_m$(LaVO$_3$)$_1$ (m=1 and 5) artificial superlattices, and in SrO[SrTiO$_3$]$_m$ (m=1 and 2) and SrO[SrCoO$_2$F]$_1$ naturally-ordered superlattices. In spite of the fact that almost all superlattices possess such highly anisotropic electronic bands created by the confinement of TM $d$ states, which is a signature of low-DET, their $PF$s are not better than that of SrTiO$_3$. The origin of this TE performance is the small weights of electronic states participating in transport, which are associated to the highly anisotropic electronic bands. The experimental evidences for the decreased effective TE performance of
quantum wells and two-dimensional electron gas systems, caused by the contribution of barrier layers used to create the confinement, support our conclusion. Another detrimental effect on TE performance is the large $\eta_t$ values along the transport direction of SrTiO$_3$ and related oxide materials, which are a factor $\sim 2$ larger than those of Fe based Heusler compounds, and a factor of $\sim 16$ larger than those of usual thermoelectrics such as PbTe. If we account for the polaronic conductivity of SrTiO$_3$, these factors are $\sim 3$ times larger. Although SrTiO$_3$ possesses highly directional TM $d$ electronic states active in transport, these states do not generate very large PF's. The origin of this TE performance is the low electron mobility as a result of the polaronic nature of electrical conductivity. In SrTiO$_3$ and related perovskite oxides, there is an important TM $d$ - O $\rho$ hybridization with covalent character, which appears to favour the polaronic conductivity. Binary TM oxides possessing high structural symmetries with stronger TM $d$ - $d$ atomic interactions, may show high anisotropy, large weights and high mobilities of the charge carriers giving improved thermoelectric performance over ABO$_3$ perovskite oxides.

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