Ph.D. Dissertation Proposal

Physics and Chemistry of ABO$_3$ Nanostructures from First Principles

Ghanshyam Pilania

Department of Chemical, Materials, and Biomolecular Engineering, Institute of Materials Science, University of Connecticut

Principal Advisor: Prof. R. Ramprasad
Associate Advisor: Prof. P. Gao
Associate Advisor: Prof. G. Rossetti, Jr.
1. Introduction

Perovskite oxides and related materials are represented by the general formula ABO₃ in which A atoms can be rare earth, alkaline earth, alkali and other large ions such as Pb and Bi that fit into the dodecahedral site of the framework.¹ The B atoms can be 3d, 4d and 5d transitional metal atoms which occupy the octahedral sites. The ideal perovskite structure is cubic although it may be somewhat distorted according to the type of the A and B cations involved. A broad diversity of the properties presented by this class of materials is derived from the fact that about 90% of the naturally occurring metallic elements of the periodic table can be synthesized in a stable perovskite oxide type crystal structure.² On one hand, these materials are of much scientific and technological importance due to their important physical characteristics such as ferroelectricity, pyroelectricity, magnetism, high temperature superconductivity and electrooptic properties which also lead to numerous attractive and diverse applications such as sensors, transducers, memories, and optical devices.³⁴⁵ On the other hand, more recently, these materials are being investigated as potential catalysts for many chemical reactions of industrial importance.⁶ Regardless of the end application these materials serve as both the testing and breeding grounds for ideas in materials chemistry and physics.

Ferroelectricity is a commonly occurring collective phenomenon in most of the perovskite oxides ⁷ arising from the competition between short-range covalent repulsions and long-range Coulombic interactions. Going from bulk to the nanoscale, these interactions will be modified and it is expected that the ferroelectric properties will be strongly affected. In fact, this was the reason that for a long time it was believed that at reduced dimensions, below a critical size, ferroelectricity vanishes due to the uncompensated surface charges on the surface which result in depolarizing fields. Recent progress in both experimental and first-principles techniques has led to advances in understanding finite-size effects in ultrathin perovskite films. Contrary to previous conventional wisdom, it was shown that the perovskite ferroelectric films can sustain a substantial polarization along the normal down to thicknesses of the order of a lattice constant,⁸⁹ provided that the depolarization field is fully compensated. It is, therefore, clear that the critical size of ferroelectricity in perovskite thin films is very sensitive towards the boundary conditions and external environment.¹⁰¹¹¹² As we move further down to zero- and one-dimensional nanostructures, finite size effects are expected to become even more prominent due to the increased surface to volume ratio and therefore one can expect even larger deviations from the bulk behavior. Whether ferroelectricity disappears in nanoparticles/nanowires or the system finds alternative ways of remaining polarized is still unclear. Furthermore, questions such as how the polarization couples with the surface relaxations, reconstructions, strain and electric field in zero and one dimensional perovskite nanostructures remain unanswered. These issues are addressed in the current
research using \textit{ab initio} computational techniques based on density functional theory\textsuperscript{13} (DFT) calculations.

From the chemistry point of view, perovskite oxides are potential candidates to be used as catalysts for a large variety of reactions such as oxidation of CO and reduction of NO in auto exhaust treatment, hydrocarbon combustion and the oxidative coupling of methane to form C\textsubscript{2} hydrocarbons.\textsuperscript{14,15} The possibility of preparing a large series of isomorphic mixed oxides by partial substitution of A and B cations \((A\textsubscript{1-x}A',xB\textsubscript{1-y}B',yO\textsubscript{3})\) which translates to a broad diversity of structure-tunability, oxygen exchange properties, excellent stability at elevated temperatures and low price compared to noble-metal catalysts makes them interesting candidates for heterogeneous catalysis.

Our knowledge of processes on perovskite surfaces during catalytic reactions is limited. The catalytic activity of the perovskite oxides has been associated with oxygen vacancies, surface adsorbed oxygen and the presence of mixed valence states of transition metal ions.\textsuperscript{16} Two different mechanisms, namely suprafacial and intrafacial, have been proposed for the catalytic oxidation reactions taking place at the perovskite surfaces.\textsuperscript{17} In the suprafacial mechanism, which is thought to dominate at low temperature, the catalyst only provides a reaction bed with the atomic orbitals of the correct symmetry and energy to activate the surface adsorbed reactant molecules while not actively participating in the reaction. In contrast, the intrafacial mechanism involves the removal of oxygen from the lattice with subsequent replenishment by adsorption of oxygen from the gas phase. Therefore, in this mechanism the catalyst actively participates in the reaction as a reagent, being partially consumed and then regenerated in a continuous cycle. In this mechanism, the rate of oxidation is markedly accelerated compared to the suprafacial catalytic reaction. Since the removal of oxygen from the lattice is an endothermic process, the intrafacial process can only dominate at high temperatures.

Experimentally, it is difficult to determine the state of the catalytic surface, the nature of the catalytically active local sites, activation barriers and geometry of the transition states during the various stages of the catalytic processes. Moreover, present knowledge of the catalytically important materials is largely based on studies (experimental and theoretical) that are performed at low temperatures and ultralow pressures. However, practical catalysts operate at atmospheric pressures and temperatures at or higher than 300 K. DFT combined with statistical thermodynamics, better known as first principles thermodynamics\textsuperscript{18,19} (FPT), can be a useful tool to address these issues. FTP has already been applied to predict the thermodynamics of oxygen adsorbed on various catalytically active noble metal and oxide surfaces.\textsuperscript{20,21} In this present work we propose to use the FPT approach to address to study catalysis on the perovskite surfaces.

We would also like to make a note here that it is very timely to undertake this study. On the one hand, recent breakthroughs in material synthesis and characterization techniques have allowed the growth of perovskite nanostructures with a control at the atomic scale and the measurements of the local ferroelectric and catalytic properties, providing experimental data for validation and comparison. On the other hand, the steady increase in computational power and improvements in the efficiency of the algorithms permit accurate first-principles study of larger and more complex systems, overlapping in size with those grown experimentally.
2. Proposed Research Plan

2.1 Research Objectives

The focus of this proposed research is to study ferroelectric and catalytic properties of perovskite oxide nanostructures using DFT based calculations. Work aimed at the following specific objectives is planned and is currently underway:

I. Ferroelectric properties of nanowires
   A. Investigation of the existence and stability of novel (e.g. “vortex”) polarization states in perovskite oxide nanowires and the development of an atomic scale understanding of the underlying driving forces that play a pivotal role in stabilizing such polarization states.
   B. Identifications of factors that control the polarization states (including possible phase transitions) by means of strain, surface terminations and electric field.

II. Catalytic properties of surfaces
   A. Development of a methodology to construct surface phase diagrams (pressure v/s temperature) for ABO₃ perovskite surfaces using first principles thermodynamics and statistical mechanics and identification of regions of the highest catalytic activities.
   B. Investigation of the thermodynamics of environment-dependent adsorption of various gases (e.g. O₂, NO etc.) on (001) AO- and BO₂-terminated perovskite surfaces, as a function of ABO₃ type (e.g. PbTiO₃ v/s LaMnO₃)

2.2 Methods

The density functional theory formalism²²,²³ forms the computational basis for all the results presented here as well as the work to be performed in the future. Within DFT, the many-electron, many-nuclei Schrödinger equation is replaced by an equivalent one-electron problem that approximates the quantum electron-electron interactions through the introduction of an effective potential, while treating classical electron-electron and electron-nuclear interactions exactly. DFT based techniques have become increasingly popular recently because they currently offer the best tradeoff between accuracy and computational efficiency with the capability of treating systems as large as ~1000 atoms.

In this project, all DFT calculations are/will be performed using the local orbital code SIESTA²⁴ and the plane wave code VASP²⁵. A typical calculation of a perovskite nanowire consisting of 97 atoms takes approximately 360 hours (15 days) on a single AMD 2.6 GHz processor. In order to finish these simulations in a tractable amount of time, calculations are performed in the Linux parallel computing environments located at the IMS, the Connecticut Institute of Supercomputing and Visualization (CISV) within the UConn School of Engineering and the NSF Teragrid.
3. Completed Work

3.1 Ferroelectric properties of nanowires

3.1.1 Existence of novel polarization states in ferroelectric perovskite nanowires

Based on the work completed so far, we have demonstrated the existence of novel polarization states in BaTiO$_3$ and PbTiO$_3$ nanowires. We find that, apart from the conventional rectilinear axial polarization state, these wires also favor a vortex polarization state in which local polarization vectors change their direction going from one unit cell to the other and form a closure polarization domain in the transverse plane of the wire. Such closure domains in ferroelectric quantum dots have also been predicted in the recent past using first principles derived effective hamiltonian techniques.

First, polarization ordering in ultrathin infinitely long free-standing BaTiO$_3$ [001] nanowires was investigated. Both stoichiometric and nonstoichiometric BaTiO$_3$ nanowires were simulated in the study. Stoichiometric nanowires contained an integral number of BaTiO$_3$ units (each with 1 Ba, 1 Ti and, 3 O atoms) with the BaTiO$_3$ units arranged in a nxn square grid along the plane normal to the nanowire axis. Owing to the stoichiometry, two of the nanowire sidewall facets were BaO terminated and the other two were TiO$_2$ terminated. The nonstoichiometric BaO-(TiO$_2$-) terminated nanowires were then constructed by adding extra BaO (TiO$_2$) layer to the stoichiometric nanowires such that the sidewall facets of the nonstoichiometric BaTiO$_3$ nanowires were either all BaO terminated or all TiO$_2$ terminated. Henceforth, the stoichiometric and nonstoichiometric (BaO- and TiO$_2$- terminated) nanowires are represented by S-nxn, BaO-nxn and TiO$_2$-nxn, respectively. For each case different sizes of nanowires with n=1 to 4 were considered. The construction of BaO-2x2 and TiO$_2$-2x2 nanowires is illustrated in Fig. 2. A comprehensive characterization of the dependence of the polarization states on the size of the nanowire and the type of the nanowire sidewall surface termination was performed. The value of the $c$ (lattice parameter along axial direction) corresponding to the most stable nanowire for each size and stoichiometry is displayed in Fig. 3 with the horizontal dashed line representing the

![Fig. 2: Schematic illustration showing construction of an infinitely long 2x2 BaTiO$_3$ nanowire with its axis along z direction. Either a Ba-centered (top) or a Ti-centered (bottom) perovskite unit cell can be used to construct the nanowire, which results in a TiO$_2$- or BaO-terminated lateral sidewalls, respectively. The nanowire with either termination will display alternating layers of PbO and TiO$_2$ planes along the axial direction.](image)
corresponding value for bulk BaTiO$_3$. Smaller $c$ values for nanowires with smaller cross sections is a consequence of the atoms (most of which are at or close to the sidewall facets) desiring to increase their reduced coordination. The $c$ value of all nanowires asymptotically approach the bulk BaTiO$_3$ value.

Regardless of nanowire stoichiometry and sidewall terminations, we predicted the presence of axial polarization in nanowires as thin as 12 Å. The tendency for ferroelectric distortion was quantified in terms of the “ferroelectric well depth,” defined as the energy difference (per BaTiO$_3$ unit) between the reference paraelectric structure and the distorted ferroelectric structure (should this be stable). In the case of the S-1x1 and S-2x2 nanowires, the only stable structures were the paraelectric ones. In contrast, the ferroelectric states were stable in S-3x3 and S-4x4 nanowires with ferroelectric well depths of 12.8 and 13.8 meV/BaTiO$_3$ unit, respectively, close to the corresponding value for bulk tetragonal BaTiO$_3$ but smaller than for bulk rhombohedral BaTiO$_3$, as shown in Fig. 4.

The off-center displacements of Ti atoms, which, in the reference paraelectric state, are at the centers of O octahedra, were used as a quantitative measure of the local ferroelectric distortions. The most remarkable polarization behavior is displayed by the TiO$_2$-4x4 nanowire, whose transverse (i.e. in plane normal to the nanowire axis) polarization distortions when further decomposed into radial and azimuthal components showed (see Fig. 5) striking vortex polarization
behavior. Although the azimuthal distortions were an order of magnitude smaller than the corresponding radial distortions, they were comparable in magnitude to the axial distortions.

Next, polarization states in nonstoichiometric PbTiO$_3$ nanowires were investigated. The choice of PbTiO$_3$ was motivated by its strong intrinsic tendency for polarization. PbTiO$_3$ nanowires were modeled in the same manner as described above for BaTiO$_3$ nanowires. A ferroelectric ground state was predicted for all PbO-terminated nanowires, while TiO$_2$-nxn (for n=1 to 3) were found to have a paraelectric ground state. For TiO$_2$-4x4, we predict a vortex ground state of ferroelectric polarization with no axial polarization. Unit cell decomposed dipole moments (calculated using Born effective charges and local ferroelectric distortions) and in-plane displacements of individual atoms with respect to a paraelectric reference state for a 4x4 TiO$_2$-terminated nanowire at zero axial strain are shown in Fig. 6. We also find that although the PbO-4x4 bears the conventional axial polarization in its ground state, a transverse vortex polarization can be stabilized by application of an axial compressive stress. In order to further clarify the nature of the “vortex polarization instability”, we carried out zone center phonon mode analysis for the TiO$_2$-4x4 nanowire with zero axial strain and the PbO-4x4 wire at -3.7% (i.e., compressive) axial strain in their respective reference paraelectric states. Presence of imaginary frequencies with their eigenvectors corresponding to the vortex instability confirmed the vortex polarization state to be the ground state.

3.1.2 Effect of axial strain and surface terminations on polarization states in perovskite nanowires

In contrast to the axial rectilinear polarization state, where polarization is purely along the axis of the nanowire and serves as the order parameter, the transverse vortex state is characterized by the existence of non-rectilinear polarization configurations within a region with the moment of the polarization (i.e., the "toroidal" moment) serving as the order parameter.
Fig. 7: Axial strain induced phase transition between non-rectilinear vortex and conventional axial polarization states for (a) TiO$_2$-4x4 and (b) PbO-4x4 PbTiO$_3$ nanowires, as predicted from the present study. Corresponding local polarizations are shown in insets. $p$ and $g$ represent polarization and first moment of polarization, respectively. The phase transition in both nanowires occur abruptly at a $c$ value of 3.87 Å, as indicated in a and b.

Our results clearly show that in both BaTiO$_3$ and PbTiO$_3$ nanowires, axial rectilinear polarization is favored by PbO sidewall terminations while TiO$_2$ sidewall terminations favor the non-rectilinear vortex polarization. Therefore, by controlling the surface chemistry one can have control over the polarization state manifested in the nanowire.

To systematically study the effect of strain on axial polarization and toroidal moment, different levels of axial strain on all TiO$_2$- and PbO-terminated nanowires were imposed by constraining the $c$ lattice parameter while allowing all other internal degrees of freedom to relax. The application of strains to the smallest three nanowires did not result in a drastic change in the manner of the polarization. However, the TiO$_2$-4x4 and PbO-4x4 nanowires responded quite differently to strain. The behavior of the TiO$_2$-4x4 and PbO-4x4 nanowires as a function of axial strain is captured in Fig. 7. It can be seen that in both cases, axial strain of the correct sign and magnitude can cause a phase transition between the pure vortex and pure axial polarization states. For instance, while the PbO-4x4 (TiO$_2$-4x4) nanowire adopts a rectilinear axial (non-rectilinear vortex) polarization state at equilibrium, an axial compressive (tensile) stress of about -3.5 % (3 %) results in the onset of an abrupt phase transition to a pure vortex (pure axial) polarization state.

We also make an interesting observation that the transition between

Fig. 8: Schematic of the polarization states in PbTiO$_3$ nanowires with axis along [001]. Depending on the strain along the nanowire axis, and sidewall surface terminations, either a vortex or a rectilinear polarization state may be favored. Arrows represent local polarization.
vortex and axial polarization states occurs at exactly the same value for the c lattice parameter (3.87 Å) along the nanowire axis for the both types of PbTiO₃ nanowires (c.f. Fig. 7). It thus appears that the c value determines the nature of polarization state. Since the c value for a given nanowire is determined by both intrinsic and extrinsic factors such as strain, sidewall terminations and passivation, these factors can be used to control the polarization state of the system. In short, axial strain and nanowire sidewall terminations crucially determine whether the polarization occurs in axial rectilinear or vortex non-rectilinear forms. The interplay between the axial strain and sidewall terminations in determining the preferred polarization state is schematically illustrated in Fig. 8.

3.2 Catalytic properties of surfaces

Before we dwell into the details of the ongoing work, it is important to note that although catalysis is not a thermodynamic equilibrium situation, equilibrium models can be particularly useful for clarifying surface compositions and reaction steps relevant to observed catalysis. In particular, the knowledge of thermodynamic phases that may exist at or close to temperature and pressure conditions of optimum catalytic performance is important for any deeper analysis.

Fig. 9: Schematic of an (001) AO-terminated ABO₃ perovskite surface in equilibrium with an oxygen reservoir, for three different values of oxygen chemical potential (µₒ). Absolute and relative surface energies (w.r.t. ideal surface) are defined in the bottom part.
3.2.1 Methodology to construct surface phase diagrams for (001) ABO\textsubscript{3} perovskite surfaces

A perovskite surface, in thermodynamic equilibrium with a gaseous environment at certain temperature (T) and pressure (P), may exhibit many possible surface structures. For instance, depending on the T, P and chemical environment the gaseous molecules may undergo physisorption, chemisorption (in molecular form), and dissociative chemisorption (i.e. breaking into atomic or sub-molecular form) on the surface, or the surface may lose some of its surface oxygen to the gas phase leaving behind surface vacancies. One can begin to understand this complexity by first looking for simplified models to describe limiting regime behavior. The first principles thermodynamics (FPT) approach is a very useful tool to quantify the thermodynamics of various surface compositional states and have been successfully and productively applied to predict the thermodynamics of many noble metal surfaces.\textsuperscript{30, 31, 32}

Based on the FPT approach, below we outline the methodology which will be used to construct surface phase diagrams of (001) AO\textsuperscript{-} and BO\textsubscript{2}\textsuperscript{-} terminated ABO\textsubscript{3} perovskite surfaces. Although this approach is quite general and can be applied to any surface in thermodynamic equilibrium with a given gaseous environment, for the sake of illustration we choose gaseous O\textsubscript{2} as the principal source of surface oxygen. For a surface in thermodynamic equilibrium with gaseous oxygen, described by the following dissociative adsorption reaction

\[
\text{Surface-}O^* \leftrightarrow \text{Surface} + \frac{1}{2} \text{O}_2 (g)
\]

where ‘\( \* \)’ represents the atomic O adsorbed on the surface and is a function of both surface O composition and configuration, one can write the following equation:

\[
\mu_O = \frac{1}{2} \mu_{O_2}
\]  \hspace{1cm} (1)

where, \( \mu_O \) is the oxygen chemical potential at a given surface coverage and \( \mu_{O_2} \) is the chemical potential of O\textsubscript{2} molecule in gas phase (assuming ideal gas behavior). \( \mu_{O_2} \) can be further expressed in terms of a reference pressure \( p^0 \) as follows:

\[
\mu_{O_2} (T, p) = \mu_{O_2} (T = 0K, p^0) + \Delta \mu_{O_2} (T, p^0) + k_B T \ln \left( \frac{p_{O_2}}{p^0} \right)
\]  \hspace{1cm} (2)

\( \Delta \mu_{O_2} (T, p^0) \) term in the above equation contains contributions from translational, vibrational and rotational degree of freedom and can be calculated using standard statistical thermodynamics results assuming the ideal gas behavior\textsuperscript{33} and \( \mu_{O_2} (T = 0K, p^0) \) is the DFT energy of an O\textsubscript{2} molecule (including zero point vibrational energy) at 0 K.

A perovskite surface, depending on the value of \( \mu_O \), may adsorb O atoms (O-rich condition) or release some surface O into gas phase (O-poor condition) or may even exist as an ideal surface (i.e. without any O vacancies or ad-atoms) as shown in Fig. 9. To obtain the stable surface phase as a function of \( \mu_O \), we first define a coverage dependent surface energy for the perovskite surface with O adatoms or vacancies with respect to the corresponding ideal perovskite surface as
\[ \Delta \gamma = \gamma(\theta) - \gamma(\theta = 0) \]  

where, \( \gamma(\theta) \) is the surface energy of the surface containing O ad-atom (or O vacancy) with a surface coverage of \( \theta \) per unit surface area and \( \gamma(\theta = 0) \) is the corresponding value for the clean surface. Then the relative surface energy for a surface with \( \theta \) O vacancy/ad-atom coverage can be given by following equations, respectively.

\[ \Delta \gamma = \gamma(\theta_{\text{vac}}) - \gamma(\theta = 0) = \frac{E_{\text{vac}}^{\theta} + 2N_O \mu_O - E_{\text{Slab}}^{\theta=0}}{2A} \]  

(4)

\[ \Delta \gamma = \gamma(\theta_{\text{ad-atom}}) - \gamma(\theta = 0) = \frac{E_{\text{ad-atom}}^{\theta} - 2N_O \mu_O - E_{\text{Slab}}^{\theta=0}}{2A} \]  

(5)

In the above equations, factors of 2 arise from the fact that the surfaces are assumed to be modeled in symmetric slab geometry with each slab having two equivalent top and bottom surfaces. \( A \) is the surface area of the slab and \( N_O \) is the number of O vacancies/adatoms on each side of the slab. The terms \( E_{\text{vac}}^{\theta} \), \( E_{\text{ad-atom}}^{\theta} \) and \( E_{\text{Slab}}^{\theta=0} \) represent the DFT energy of the appropriate slab geometries and can be directly calculated from first principles calculations. Also note that a plot between \( \Delta \gamma \) and \( \mu_O \) will be a straight line with a slope of \( \theta \) (positive for vacancies and negative for O ad-atoms). Using the above two equations for the various coverages (\( \theta \)), one can, in principle, calculate the critical values of \( \mu_O \) for which the surface in equilibrium with \( \text{O}_2 \) gas switches from one vacancy/O ad-atom coverage to the other, as shown schematically in Fig. 10 for a few limiting coverages. It is evident from the figure, as chemical intuition would also suggest, that at very low levels of oxygen chemical potential \( \mu_O \) (i.e. \( \mu_O < \mu_1 \)) a 100% vacancy coverage will be favored on the surface while for a very high \( \mu_O \) situation (i.e. \( \mu_O > \mu_4 \)) all the adsorption sites on the surface will be occupied by O ad-atoms. At the intermediate values of \( \mu_O \) surface switches from dilute limit O vacancy coverages to dilute limit O ad-atom coverages. For \( \mu_O \in (\mu_2, \mu_3) \) a clean surface without any O vacancy or ad-atoms will be thermodynamically stable. With the knowledge of the critical oxygen chemical potential (\( \mu_i \)) values for which thermodynamic stability of the surface switches between two surface phases containing different levels of vacancy (ad-atom) coverages (let’s say \( \theta_1 \) and \( \theta_2 \)), we can then find the corresponding boundary on the surface phase diagram by combining Eq. (1) and Eq. (2) as follows.
A schematic illustration of a pressure-temperature surface phase diagram for a AO-terminated surface in thermodynamic equilibrium with O$_2$ gaseous environment.

\[
\mu^{\theta_0\rightarrow\theta_2}_O(T,p) = \frac{1}{2}\left[\mu_{O_2}(T = 0K, p^0) + \Delta\mu_{O_2}(T, p^0) + k_B T \ln\left(\frac{p_{O_2}}{p^0}\right)\right]
\]

A schematic of the resulting surface phase diagram from the above analysis is shown in Fig. 11 which shows the stability of various surface phases (O vacancies, O ad-atoms and clean surface) as a function of temperature and O$_2$ partial pressure.

4. Proposed Work

4.1 Electric field response of the vortex polarization state in PbTiO$_3$ nanowires

After studying the effect of strain and surface chemistry on the vortex state of polarization in ABO$_3$ nanowires, a natural extension of the present work will be to investigate its response towards the applied external electric field. A knowledge of the dielectric response under one-dimensional confinement would be useful from both scientific and applied points of view.

In this proposed work, dielectric and piezoelectric properties, dynamic effective charges and response towards the applied electric field for different sizes of PbO-nxn and TiO$_2$-nxn (with n=1 to 4) PbTiO$_3$ nanowires will be determined using density functional perturbation theory (DFPT).$^{34}$

Polarization v/s applied electric field (P v/s E) plot for the TiO$_2$-4x4 nanowire containing vortex polarization state will be calculated by relaxing the nanowire in the presence of different levels of applied external electric fields. The dipole moment perpendicular to the wire axis in the final energy minimized relaxed geometry will be used to calculate the transverse polarization. The external transverse electric field (normal to the wire axis) will be applied by introducing an artificial dipole layer in the supercell. The applied external electric field will then be varied by varying the dipole moment density of the dipole layer. The P v/s E plot for the PbO-4x4 nanowire in its ground state (containing only axial polarization) will also be determined in the similar way.
Finally, the results for the two nanowires will be compared to understand the response of the vortex polarization state towards the external applied electric field.

4.2 Thermodynamics of environment dependent interaction of various gases on the (001) surface of ABO₃ type perovskites

Present knowledge of the catalytically important materials is largely based on studies (experimental and theoretical) that are performed at low temperatures and ultralow pressures. However, in practice catalysts operate at atmospheric pressures and temperatures at or higher than 300 K. In this proposed work, using the approach described in the section 3.2.1, we plan to construct phase diagrams of surface structures in the (T, p) space from ultrahigh vacuum to technically relevant pressures and temperatures for both AO- and BO₂-terminated surfaces of catalytically important perovskite such as LaMnO₃ in equilibrium with various gases (e.g. O₂, N₂, NO etc.).

The choice of the various gaseous environments is based on the underlying motivation of investigating various perovskites as sorbents or catalysts for trapping or destroying NOx species e.g., in DeNOₓ processes. A necessary step in developing a more complete description of perovskite catalyzed NO oxidation is enumeration and description of the various surface species relevant to the catalysis. In the proposed study, we plan to use large supercell DFT simulations to characterize the stable and some metastable states (in terms of adsorption site, equilibrium geometry, electronic structure, energetics etc.) of adsorbed NO, N₂, and O₂ on a LaMnO₃ (001) surfaces with LaO and MnO₂ terminations. We propose to use two limiting surface coverages, namely a 100% coverage (corresponding to one adsorbed molecule per unit cell on the surface) and a dilute limit coverage (when adsorbed molecules are far apart from each other on the surface), of adsorbed species on the surface. Charge density and local electronic structure analyses will be used to characterize the nature and extent of interactions between the adsorbates and the surfaces considered. An attempt will also be made to extend the thermodynamic picture in order to address the kinetics of NOₓ interactions with ABO₃ surfaces.

5. Impact of Work

Currently, ferroelectric perovskite oxides are under active investigation for the possibility of their potential use in next generation nonvolatile random access memory (NVRAM). A very high information storage density can be achieved (10⁵ times greater than the present state of the art) by storing individual bits of information in terms of local polarization states in ferroelectric perovskite nanostructures.

Our work exploring novel polarization states in BaTiO₃ and PbTiO₃ nanowires, for the first time using parameter free ab initio computation, provides a clear evidence of the existence of vortex polarization states in one-dimensional ferroelectric nanostructures. The minimum size of the ferroelectric nanowires showing the low-temperature vortex-type polarization bistability (clockwise and counter-clockwise) is determined to be 1.6 nm. If each of such individual vortex state (involving few hundreds of atoms) can be successfully used to represent a bit of information (in terms of 0 or 1) in a controlled manner, it immediately enables an ultimate NVRAM density of
five orders of magnitude larger than those currently available. Although challenges regarding speed, long term stability and dense integration still remain, it certainly brings us one step closer to Feynman’s vision. We also hope that our computational results will motivate experimental efforts in these directions.

The second part of the proposed work is a first step towards evaluating the feasibility of using perovskite surfaces to remove nitrogen oxides (NOx) in exhaust gases. NOx species are formed in industrial combustion systems and automotive engines when air is used as an oxidant. In the atmosphere, nitrogen oxides are a serious health hazard for the human respiratory system and contribute to the generation of smog and acid rain. They are among the most harmful environmental pollutants. Perovskite oxide surfaces are currently being investigated as sorbents or catalysts for trapping or destroying NOx species i.e., DeNOx processes. To improve the performance of DeNOx operations one needs a fundamental atomic level understanding of the surface chemistry of NO on these materials.

The main prerequisites for reaching a microscopic understanding of the DeNOx processes (or heterogeneous catalysis in general) are the identification of the composition and geometry of the catalyst’s surface and the determination of the various chemical reactions that take place under realistic conditions. Unfortunately, most surface science experimental techniques are difficult if not impossible to use at the pressures (of the order of 1 atm) and temperatures (often higher than 300 K) that are typically applied in steady state catalysis. Therefore, what is considered to be important elementary processes at the catalyst’s surface (e.g., dissociation, diffusion, and chemical reactions) has usually been concluded from chemical intuition and extensive knowledge from ultrahigh vacuum (UHV) experiments. The work undertaken in the present study is an important first step towards reliably bridging the temperature and pressure gap between “idealized surface science work” and “real life”. The knowledge of (T, p) space phase diagram for perovskite oxide surfaces will provide insights regarding the regions where catalysis may be most efficient, which will, hopefully, be further useful for designing experiments.
6. References