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Multimodal quantitative analysis of functional materials: STEM and DFT EELS simulation

Pranjal Nandi

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Doctoral Thesis

**Multimodal quantitative analysis of
functional materials: STEM and DFT
EELS simulation**

Author:

Pranjal Nandi

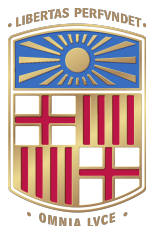
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Multimodal quantitative analysis of functional materials: STEM and DFT EELS simulation

Memòria presentada per optar al grau de doctor per la

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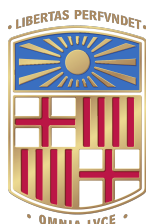
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To every hand that helped, every voice that encouraged, and every silence that gave me space
to grow ...

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Keywords

Transmission Electron Microscopy (TEM)

Scanning Transmission Electron Microscopy (STEM)

High-Angle Annular Dark Field (HAADF)

Electron Energy Loss Spectroscopy (EELS)

Energy Loss Near Edge Structure (ELNES)

Density Functional Theory (DFT)

Multislice Simulation

STEM Image Simulation

Dielectric Function

Antisite Defects

ATOMAP

EELS Simulation

Chapter 1

General introduction and objectives

Transmission Electron Microscopy (TEM) has transformed materials science through the ability to directly view atomic structures. From Ruska and Knoll's original ideas [1], TEM has evolved from a mere imaging technique to a full analytical workstation. Through advances such as aberration correction [2], cold field emission sources [3], and ultra-stable monochromators [4], modern instruments are now capable of easily achieving sub-angstrom resolution and detecting picometer-scale displacements. Scanning Transmission Electron Microscopy (STEM), for instance, supports element-sensitive contrast utilizing detectors such as High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF), providing Z (atomic number) - contrast imaging that is ideal for the identification of single atomic columns [5, 6]. Spectroscopic tools such as Electron Energy Loss Spectroscopy (EELS) allow us to examine materials' chemistry, and electronic properties. These are greatly valued when exploring functional oxides, semiconductors, and nanostructures in which the local behavior at the atomic level determines overall characteristics.

The growing interest in TEM studies over the past few decades is mainly driven by major technological advancements [7]. TEM is no longer restricted to vacuum static imaging but is extensively used today in dynamic in situ experiments, where researchers are able to perform experiments on materials under gas flow, liquid state, or external stimuli like temperature, biasing, or light [8]. Such advances have tremendously broadened the areas of TEM ap-

plication in nanotechnology, catalysis, battery studies, soft matter, and even in biological and medical sciences [9, 10]. In addition, combination with direct-electron detectors and advanced machine learning algorithms for data analysis, has improved resolution and speed, further expanding the limits of what TEM can achieve [11].

Despite these strengths, interpreting experimental images and spectra is a complex task. Image contrast depends sensitively on parameters like sample thickness, defocus, aberrations, and dynamical scattering, which complicate direct analysis. To address this, simulations serve as an essential interpretation tool. For example, the multislice method of STEM image simulation, by considering the wave propagation of electrons through a crystal model divided into slices, provides realistic images that can be compared with experimental images [12]. These simulations help confirm structural models by predicting how a given arrangement should appear under specific imaging conditions. Likewise, Density Functional Theory (DFT) has long been a standard for simulating electronic structure and optical response. DFT simulations provide insights about the electronic structure, material properties, and chemical processes, supporting both fundamental research and technological development. It also enables simulation of EELS, including fine structures such as Electron Energy Loss Near Edge Structure (ELNES), allowing researchers to distinguish oxidation states and chemical environments [13, 14]. Meanwhile, image analysis tools such as ATOMAP [15] enable the determination of atomic column positions and shapes in STEM images, even when the images contain many columns composed of a variety of atomic species with large intensity differences. Together, these tools provide a synergistic framework, where experimental observations are supported by simulation and quantitative analysis, enabling a deeper understanding of both crystal structures and electronic interactions.

This thesis is driven by the motivation of advancing the interpretation of transmission electron microscopy data through the simulation of STEM images and DFT (EELS) spectra. By focusing on how atomic configurations and bonding environments influence contrast in TEM/STEM and spectral features in EELS, the work contributes to a deeper understanding of the data obtained through electron microscopy. The approach is applied across a variety of materials of high technological interest.

The objectives of the thesis are as follows:

1. Introduce and establish the theoretical and computational frameworks for STEM imaging and EELS simulations.

By explaining the main theoretical concepts and computational approaches used in the thesis, we aim to establish the foundation for the analyses carried out to solve specific materials science problems. We will describe the process of image simulation using multislice techniques, present STEM image analysis techniques using ATOMAP, and describe the theoretical underpinnings of DFT and how it is used to simulate EELS spectra and ELNES features.

2. Investigate the influence of oxygen stoichiometry and structural phase transitions on the dielectric properties of hafnia-based resistive memory devices.

The objective is to comprehend the structural alterations brought about by oxidation in hafnium oxide compounds, such as phases transition from rhombohedral to monoclinic, and its impact on the dielectric characteristics of Resistive Random Access Memory (RRAM) devices through the comparison of DFT simulations with experimental STEM and EELS data. This knowledge will help link local atomic structural transformations with dielectric performance, contributing to the design of next-generation memory materials.

3. Examine the effects of pressure and charge on the EELS spectral features of xenon gas clusters.

The aim is to evaluate the effects of changes in external parameters, namely electronic charge and pressure, on the electronic structure and associated spectral signatures in confined Xe₂ and Xe₅ clusters. Changes in the M_{4,5} edge will be interpreted using DFT-based EELS simulations. These insights are essential for the interpretation of EELS spectra in systems where small changes in environment can lead to measurable spectral shifts.

4. Develop a methodology to quantify antisite defects in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) using STEM image simulations and intensity analysis.

This goal is to quantify antisite defect densities in LSMO using a Relative Intensity Ratio (RIR) metric by combining multislice simulations, ATOMAP analysis, and HAADF-STEM imaging. In order to comprehend trends in defect formation, this technique will be used on LSMO thin films that have been synthesised under various oxygen partial pressures. Understanding defect distributions as a function of synthesis conditions, such as oxygen partial pressure, can help optimise the performance of LSMO in solid state electrochemical devices.

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Chapter 2

Methodology: image analysis, simulation, and DFT-EELS

This chapter provides an introduction to the fundamentals of image analysis and simulation methodologies that are used in conjunction with experimental measurements obtained from transmission electron microscope (TEM), to perform sample characterisation. It begins with the use and applications of image analysis, followed by the theory behind the simulation of Electron Energy Loss Spectroscopy (EELS) using Density Functional Theory (DFT) calculations.

2.1 Image analysis

Scanning Transmission Electron Microscopy (STEM) image analysis is essential for understanding material properties at the atomic scale, providing both qualitative and quantitative insights into structural features. It enables the identification of defects such as vacancies, dislocations, and antisite defects, which play a critical role in determining a material's electronic and mechanical behaviour. Image analysis done on the images obtained from different modes, such as high-angle annular dark field (HAADF) and annular bright field (ABF) (mostly used in this thesis), enables researchers to infer crucial information about atomic structures [1]. Structural quantitative characterisation can be carried out through measurements, such as interplanar spacings [2, 3], strain [4], defect densities [5, 6], and atomic column intensities [7]. This capability is particularly valuable for studying materials with complex microstructures, including nanomaterials and heterostructures. The analysis also helps elucidate how various imaging conditions such as electron dose [8], defocus [9], and aberrations [10] affect the observed contrast and resolution in TEM images.

Modern TEM analysis relies on specialised software platforms that streamline image processing, quantitative analysis, and visualisation. These tools range from proprietary software like Digital Micrograph [11] or Nion Swift [12], Eje-Z [13, 14] to open-source packages such as ATOMAP [2], each tailored to specific aspects of image analysis. With respect to the focus of this thesis, the software ATOMAP has been used extensively for image analysis.

2.1.1 ATOMAP

ATOMAP is an open-source Python-based tool for analysing high-resolution STEM images. It is designed specifically to identify atomic column positions and calculate significant information, which are essential for quantitative studies of atomic arrangements, defects, and strain in materials [2]. ATOMAP combines advanced image processing algorithms and statistical methods, making it highly effective for precise and automated atomic-scale analysis. Some of its most relevant characterisation capabilities are as follows.

- **Atomic Column Detection:** ATOMAP uses Gaussian fitting to locate the centers of atomic columns in STEM images. This technique is based on the assumption that atomic columns appear as Gaussian-shaped intensity peaks in HAADF-STEM images, with the position of each peak corresponding to an atomic column. Gaussian fitting enhances the precision of atomic position determination, as the fitted peak's centroid provides sub-pixel resolution.
- **Atomic Lattice Mapping:** Once the atomic columns are identified, ATOMAP can map the lattice structure by analysing the positions of these atomic columns relative to each other. This lattice mapping step is essential for determining local variations in atomic spacing, which can indicate strain, defects, or compositional variations.

In materials with multiple atomic sub-lattices (such as compounds with different atomic species), ATOMAP can identify and distinguish each sub-lattice. This differentiation allows users to study complex materials where the arrangement of the different sublattices determines the material properties, such as perovskite structures.

- **Atomic Column Intensity Profiling:** In HAADF-STEM images, the intensity of atomic columns is correlated with atomic number (Z-contrast), allowing for compositional related analysis. ATOMAP profiles these intensities to estimate elemental composition or detect changes in occupancy in atomic columns, which is especially useful in studying doped materials or alloys.
- **Ellipticity:** In many HAADF-STEM images, the shape of the columns can also provide important information about the atomic arrangement. Small shifts of the atoms perpendicular to the projection direction result in elongated column shapes. Ellipticity in ATOMAP is calculated by fitting an ellipse to atomic columns from the STEM images. The software calculates the optimum-fit ellipse for sets of atoms to facilitate precise determination of values of ellipticity. Quantitative information about every atomic column in the form of orientation of the major axis of the fitted 2D gaussians and the major to minor axis ratio is also extracted. These values are directly interpretable in the case of HAADF-STEM images as two overlapped atomic columns.

- **Vector Mapping:** From the lattice mapping, ATOMAP calculates vectors between neighbouring atomic columns to analyse distortions like polar off-centering, polarisation gradients, and ferroelectric or antiferroelectric phase transitions.

To illustrate the image analysis performed by ATOMAP, we provide here a brief example, an analysis of a $\text{BiFeO}_3/\text{LaFeO}_3$ (BFO/LFO) multilayer system. The samples were provided by the team of Dr. Pascal Ruello from the Institut des Molécules et Matériaux du Mans (UMR 6283 CNRS), Le Mans Université, and these samples are used for Terahertz (THz) photonics [15] and photovoltaic responses [16]. The BFO/LFO superlattice has been grown with Pulsed Laser Deposition (PLD). In total, 15 bilayers of BFO/LFO have been grown on a strontium titanate substrate for a superlattice thickness of around 60 nm. High Resolution TEM (HRTEM) images and diffraction patterns were obtained in the JEOL 2010F of the CCI-TUB, working at 200 kV and HAADF-STEM images were obtained in a FEI Titan3 G2 in CentraleSupélec (Université Paris-Saclay) working at 300 kV.

Fig. 2.1(a) shows the HRTEM image of the BFO/LFO sample. Figs. 2.1(b) and 2.1(c) show the corresponding Fast Fourier Transforms (FFT) and the intensity profiles along the arrows marked in the FFT, respectively. Fig. 2.1(d) presents the selected area electron diffraction (SAED) pattern, and Fig. 2.1(e) shows the intensity profile along the arrows marked in the SAED pattern, parallel to the growth direction. The preliminary analysis from FFT (Fig. 2.1(b)) reveals the presence of multilayers with two types of periodicity, one with $1/12$ that arises from the succession of 6 unit cells of BFO and 6 of LFO and another periodicity of $1/24$, which would imply a doubling of periodicity. The intensity profile from the SAED pattern (Fig. 2.1(e)) also reveals the same. The origin of this phenomenon couldn't be directly observed in the HRTEM or HAADF-STEM images. This is where ATOMAP was utilised on HAADF-STEM images. At first, ATOMAP is fed the data to locate the various atomic columns (A site and B site in this case) as shown in Fig. 2.2. Once it is done, the ellipticity of the Bi atomic positions (Fig. 2.3(b)) showed a periodic pattern that could be linked to the Bi atoms zig-zagging, resulting in an elliptical atomic column. The ellipticity of the Bi positions is in good agreement with the Pnma antiferroelectric structure proposed

in [17]. Plotting the main axis of the ellipse (Fig. 2.3(a)) shows that the ellipticity pattern is not simply repeated after one BFO/LFO bilayer (which has a period of Λ). Instead, it repeats after two bilayers (2Λ) [15], resulting in a superlattice of 24 unit cells, which explains the electron diffraction and HRTEM FFT observed reflections. This example shows how image analysis is an indispensable tool in the understanding of materials at the atomic level.

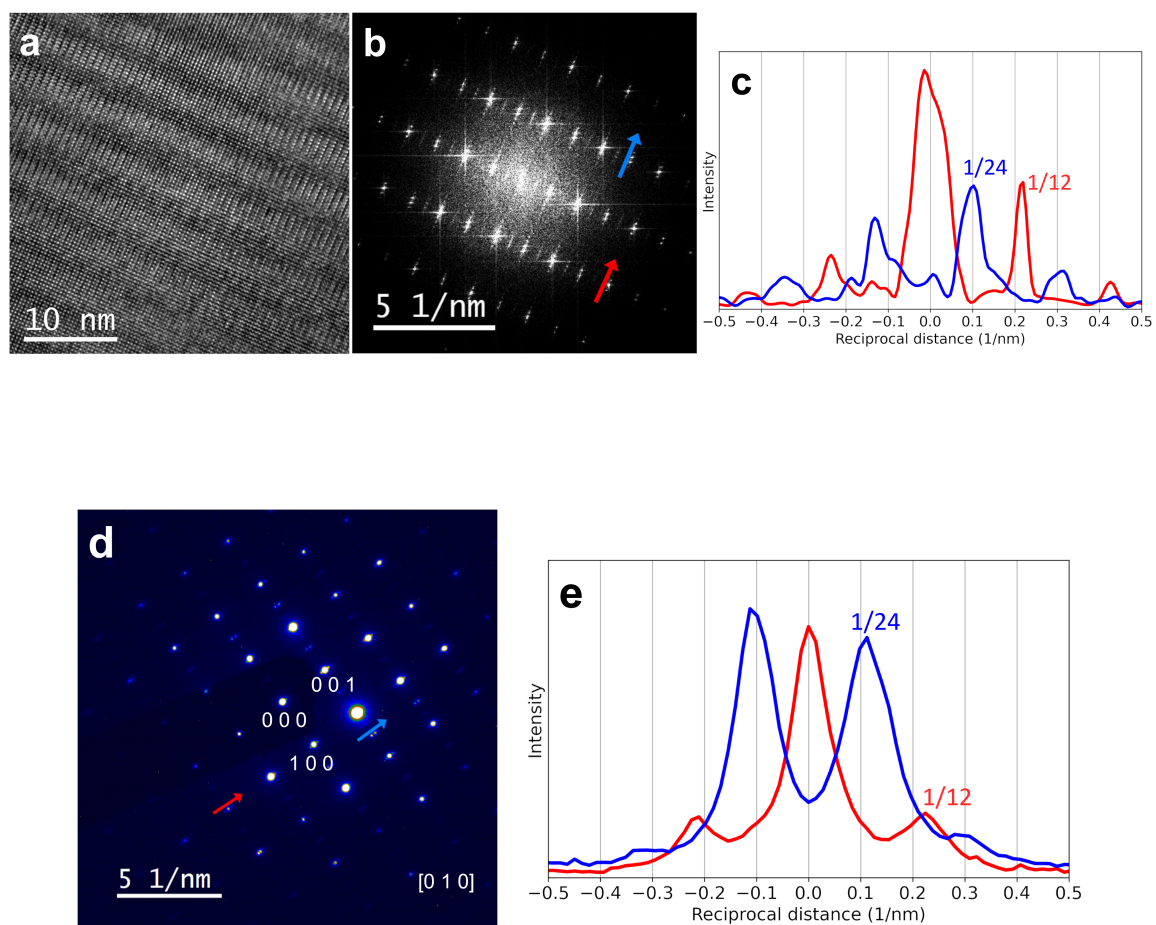


Fig. 2.1 BFO/LFO superlayer depicting the emergence of lattices with different orders of periodicity as per the experimental findings. (a) HRTEM image, (b) FFT, and (c) intensity profile along the corresponding arrows in the FFT. The first satellites of the red profile correspond to 1/12th of the unit cell spot, while the blue peaks are placed at 1/24th of the same reciprocal distance. (d) Diffraction pattern (indexed as pseudocubic symmetry) and (e) the intensity profile along the arrows marked on the diffraction pattern.

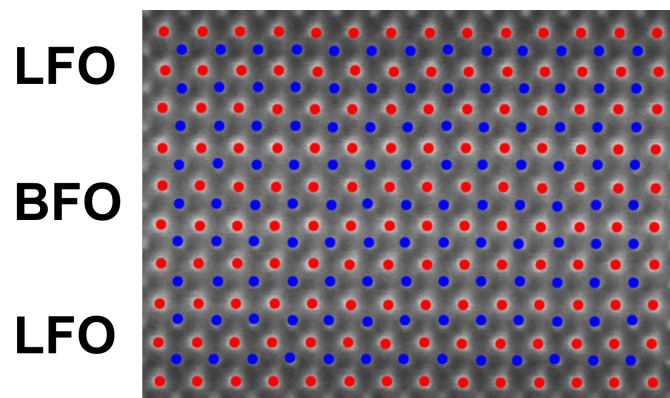


Fig. 2.2 Detection of atomic columns (A site in red, B site in blue) of the BFO/LFO sample using ATOMAP.

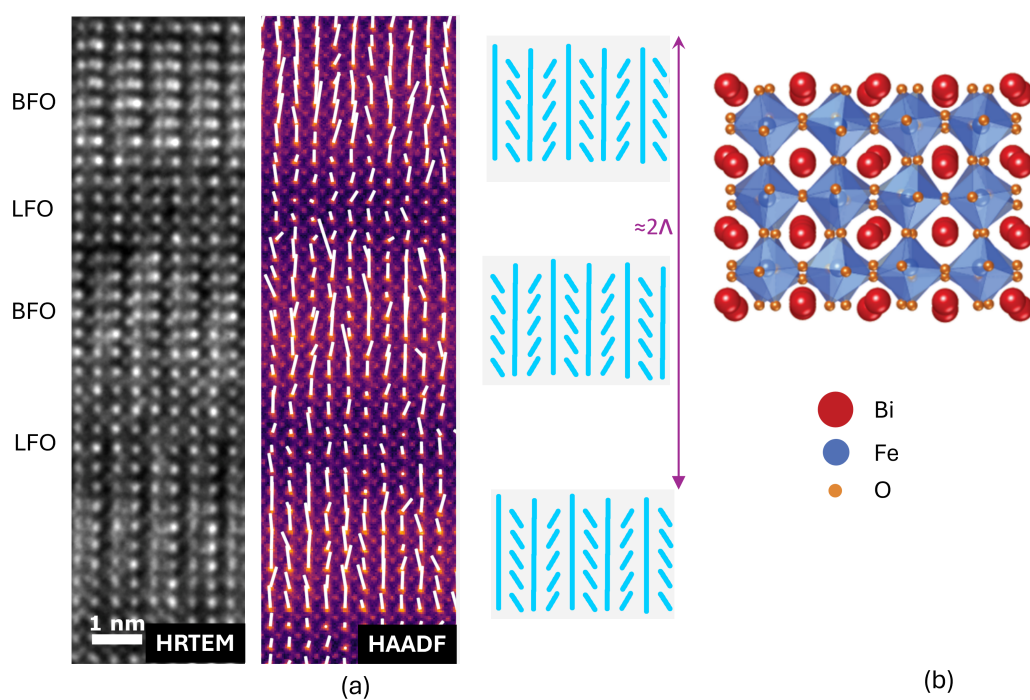


Fig. 2.3 (a) Multiple structural order detection in a BFO/LFO superlattice using ATOMAP. HRTEM image (left) and A-site displacements (by ellipticity in ATOMAP) (middle) extracted from a HAADF-STEM image obtained at 300 kV acceleration voltage. The sketch on the right panel depicts the non-equivalence of the Bi displacement (light blue lines) between two adjacent BFO layers. (b) The crystalline structure of BFO, showcasing the double structural order in the Bi orientations.

2.2 Why do we need image simulation

Interpreting STEM images is often complex due to multiple scattering effects, contrast transfer functions, electron phase interactions, and specimen thickness variations [18]. To overcome these challenges and better understand experimental STEM images, STEM image simulation has become an essential tool in materials science, namely in nanotechnology, functional oxides and semiconductor research. It provides theoretical images based on known structural models, enabling researchers to validate their experimental observations, refine material properties, and interpret complex image features [19].

Simulations help in deconvoluting these effects to extract meaningful structural and compositional information. Simulated images act as a reference, making it easier to distinguish real material features from artefacts introduced by experimental conditions [20]. Another advantage is the verification of atomic structures. By comparing simulated images with experimental ones, researchers can validate structural models of unknown materials, including crystal structures, defects, and interfaces.

2.3 Fundamentals of image simulation

Over the years, STEM image simulation has evolved significantly, with advances in both computational algorithms and hardware, making demanding simulations increasingly accessible. The core principles of STEM image simulation have remained largely the same, but improvements in model accuracy, potential calculation, and electron propagation methods have transformed the field. The two most common methods of STEM image simulations are the Bloch Wave Method [21, 22] and the Multislice Method [23, 24]. The Bloch wave method utilises Bloch waves to describe the propagation of electrons through a periodic crystal lattice. This method is particularly well-suited for small, periodic unit cells and provides highly accurate results for diffraction simulations. The multislice method involves dividing the specimen into thin slices and simulating the electron wave's transmission and propagation through each slice sequentially. It uses fast Fourier transforms to compute the evolution of the electron wave function between slices, making it suitable for large-scale

simulations. The image simulation process typically includes model creation, potential generation, wave propagation, image formation, and post-processing in the order as shown in Fig. 2.4. In the following sections, each of the steps for such a simulation will be explained.

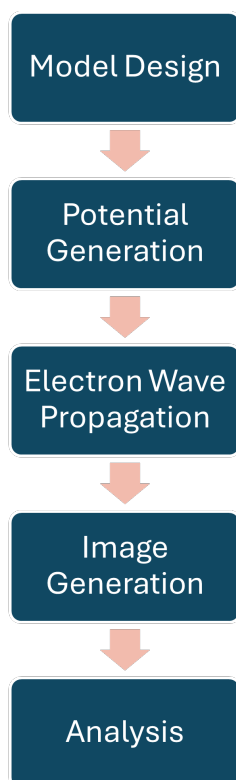


Fig. 2.4 Flow chart depicting the steps for STEM image simulations.

2.3.1 Model design

The model design starts by obtaining the crystallographic data from the crystallographic databases, usually in the form of CIF (Crystallographic Information File). This file provides the lattice parameters and atomic positions within the unit cell, essential for building a periodic model of the crystal. In cases where the crystal data is not available, it can be built manually using multiple softwares such as Vesta [25] and Atomic Simulation Environment [26].

Once the basic structure has been built, depending on the interest of the study, the structure is modified to incorporate changes such as vacancies, defects, dislocations and is used for the next steps. These features affect the local scattering potential and influence

image contrast. In polycrystalline materials or heterostructures, it's important to include grain boundaries or interfaces, as these regions exhibit distinct electronic and structural properties.

Following the introduction of the changes in the structure, structural relaxation is often performed to allow atoms to find their lowest energy configuration, which minimises any artificial stress introduced during defect incorporation. This is usually done by performing Density Functional Theory (DFT) calculations. These methods refine the atomic positions, to provide a realistic model that accurately simulates electron scattering effects.

2.3.2 Potential generation

Potential generation involves defining how the atomic structure of the sample interacts with the incident electron wave by calculating the scattering potential at each atomic site. The primary purpose of potential generation is to produce a static map of scattering potentials that align with the atomic positions in the sample. This scattering potential represents the electrostatic field produced by the atomic nuclei and surrounding electron cloud of each atom. The resulting potential map forms the basis for simulating electron scattering within the material. Although this map remains constant throughout the simulation, it underpins the interaction between the electron wave and the sample. The multislice approach of generating potentials is one of the most used methods for such tasks. In this method, the phase shift for each slice is calculated separately, based on the atomic potentials within that slice. This approach is critical in thick samples where dynamical scattering effects become significant, as it models the cumulative effect of electron scattering through each layer.

2.3.3 Electron wave propagation (multislice simulation)

Electron wave propagation is a critical step in the process of multislice STEM image simulation. It is the stage where the electron wave interacts dynamically with the sample atomic structure, based on the scattering potentials defined in earlier steps. The multislice method captures dynamical scattering effects [27] and interference patterns that arise from the electron wave interacting with atoms at various depths, which is essential for accurately simulating high-resolution STEM images.

Traditional approximations, like the kinematic theory, assume only single scattering events and therefore are insufficient for high atomic number materials or thicker samples where multiple scattering events are significant. In the multislice approach, the sample is divided into a series of thin, parallel slices, each representing a specific atomic layer or a group of layers as shown in Fig. 2.5. The electron wave is modified as it propagates through each slice, capturing the complex scattering effects that arise from the material's structure.

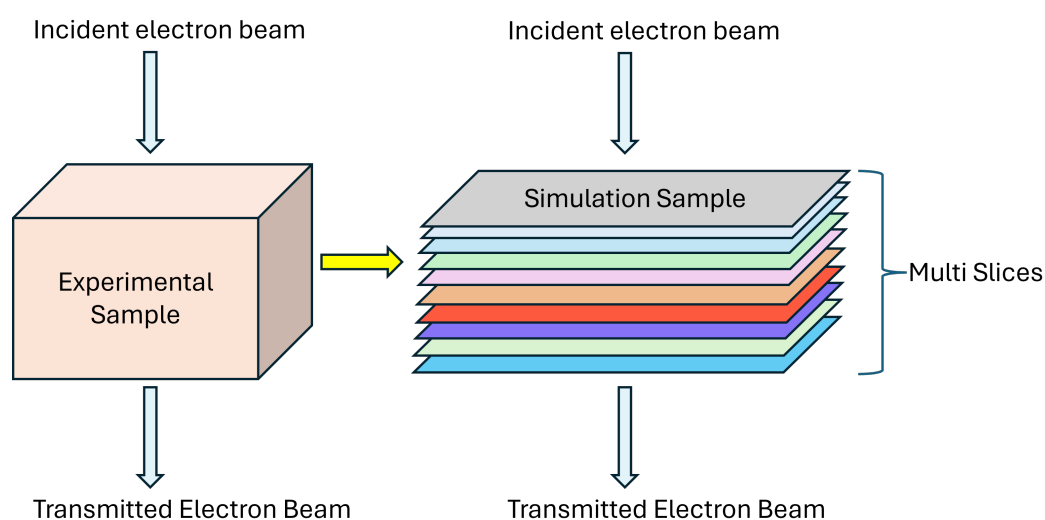


Fig. 2.5 Conversion of an experimental sample into its equivalent multislice sample for simulation.

The initial electron wave function, $\psi_0(r)$, represents the coherent, plane electron wave entering the sample. This wave function is defined based on parameters such as the electron accelerating voltage and incident beam coherence. For example, a typical accelerating voltage for high-resolution STEM is around 300 kV, which corresponds to an electron wavelength of approximately $0.0197 \text{ \AA}$, enabling resolutions sufficient to resolve atomic spacings in most crystalline materials [20].

At each slice, the electron wave undergoes a phase shift due to the electrostatic potential generated by the atomic structure within that layer. This phase shift is governed by the projected potential of the atoms in the slice, denoted as $V(r)$, and is calculated based on the

atomic scattering potentials previously generated. The phase shift imparted by each slice is described by the transmission function $T(r)$:

$$T(r) = \exp\left(i\sigma \frac{V(r)}{\lambda}\right),$$

where σ is the interaction constant (dependent on the electron wavelength and accelerating voltage) and λ is the electron wavelength. The function $T(r)$ applies a phase modulation to the wave function according to the electrostatic potential of each slice, effectively representing the impact of atomic structure on the electron wave [19].

After interacting with the potential in a slice, the electron wave is propagated to the next slice using a free-space propagation function. This propagation accounts for the distance Δz between slices and involves calculating how the electron wave diffracts over that distance. In Fourier space, this propagation is represented by a propagation operator $P(k)$, which applies a phase factor corresponding to the free-space travel distance:

$$P(k) = \exp\left(-i\pi \frac{\lambda \Delta z}{k}\right),$$

where k is the spatial frequency vector in Fourier space. The propagation operator effectively translates the electron wave from one atomic layer to the next, with phase alterations that model diffraction effects over the slice thickness. This operation is repeated for each slice, building up the cumulative effect of electron scattering through the entire thickness of the sample [27].

The propagation and phase-shifting process is iterated over all slices, building up a cumulative interaction between the electron wave and the sample. At each step, the wave function $\psi_n(r)$ is transformed by applying the phase shift from the transmission function $T(r)$ and then propagated using the operator $P(k)$. This iterative process captures dynamical scattering effects, where the electron wave repeatedly scatters within the material, leading

to complex interference patterns and contrast features in the final image. Such dynamical effects are particularly important for thick samples and materials with heavy atoms, such as transition metal oxides [19]. The resulting exit wave function is then used in the image generation process.

2.3.4 Image generation

Once the electron wave exits the sample, the simulated image formation step models how the microscope's optical elements, such as the objective lens and aperture, transform the electron wave into an intensity distribution that corresponds to the observed STEM image.

The objective lens in a STEM introduces various aberrations, including defocus, astigmatism, coma, spherical and chromatic aberrations, which distort the electron wave. Correcting for these aberrations is crucial for high-resolution imaging and is simulated using objective lens transfer functions. The contrast observed in STEM images is also influenced by phase shifts introduced by the said lens. All of these must be taken into account in this step.

Beyond the sample, several detectors such as bright field (BF), high angle annular dark field (HAADF), annular dark/bright field detectors (ADF/ABF) or even segmented detectors can be simulated by choosing the angular range of electrons that will form the simulated image. HAADF and ABF modes are particularly useful in distinguishing between atoms of different atomic masses, with HAADF favoring heavier elements and ABF allowing the visualisation of lighter atoms.

For all the image simulations in this thesis, the software Dr. Probe [24] has been used. It is based on the multislice algorithm and features the frozen-lattice method for simulating thermal diffuse scattering by averaging over many random atomic displacements, which is critical for accurate atom counting and bias prevention in high-resolution simulations. The various settings used for the simulations are explained in the relevant chapter. To illustrate the use of detectors and image simulations, an example is included in the following paragraph.

$\text{YBa}_2\text{Cu}_3\text{O}_7$ is a high-temperature superconducting oxide with a layered perovskite structure, widely studied for its exceptional electronic properties [28–30]. Its complex atomic arrangement, consisting of alternating layers of heavy (Ba, Cu, Y) and light (O) elements

as shown in Fig. 2.6(a), makes it suitable for evaluating contrast mechanisms and imaging capabilities in STEM. An example of STEM image simulation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ is presented in Fig. 2.6(b,c). In this study, a crystallographic supercell was first constructed to represent the atomic arrangement, and STEM image simulations were subsequently performed. The simulated images clearly demonstrate the contrast sensitivity of different detectors: in the HAADF mode as shown in Fig. 2.6(b), only the heavier elements (Ba, Cu, Y) are distinctly visible due to the Z-contrast mechanism, whereas in the ABF image as shown in Fig. 2.6(c), the lighter oxygen atoms are also resolved, showcasing the technique's capability to capture low-Z elements. The iterative nature of the multislice method enables the realistic simulation of STEM images by accurately capturing the structure and composition of the sample. This approach is particularly effective for materials with complex atomic structures or high atomic numbers, as it accounts for cumulative phase modulation across layers. This is crucial for interpreting lattice strain, atomic positions, and defects, providing insights into the material's magnetic and electronic properties, thereby making this method an essential tool for STEM image simulation [18]. Such simulations not only validate the theoretical expectations but also serve as a benchmark for interpreting experimental STEM data. They contribute significantly to our understanding of the imaging process and structural identification in complex oxides, especially in the context of functional materials like superconductors.

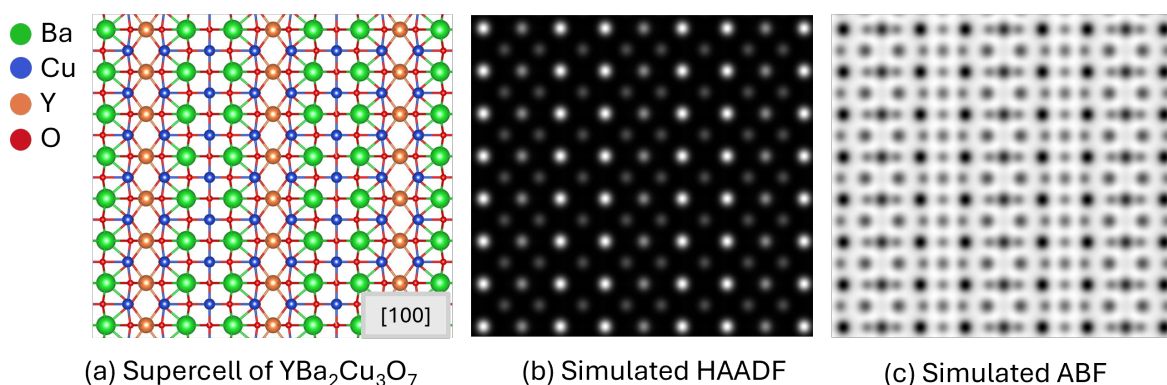


Fig. 2.6 Simulation of STEM imaging of (a) supercell of $\text{YBa}_2\text{Cu}_3\text{O}_7$, its corresponding HAADF simulation (b) and ABF simulation (c) .

2.4 Why do we need DFT

The study of nanomaterials, particularly crystalline and polycrystalline materials typically involves the study of several atoms, usually periodically arranged in a particular order referred as a quantum system. The theoretical study of these quantum systems is a complex field as they stand as a many body problem having multiple properties such as dual wave/particle like behaviour, existence in multiple states simultaneously, time dependent change of states or, interaction with the electronic charges of electron beams. Unlike classical mechanics, which can predict the motion of macroscopic objects with certainty, quantum mechanics deals with the inherently probabilistic nature of subatomic particles. This introduces unique challenges in characterising the behaviour of particles at the quantum level. In order to solve them, the Schrödinger equation provides a mathematical framework for understanding and predicting the behaviour of quantum systems in diverse contexts [31]. The equation addresses the particle duality through wave functions, which encapsulate the probabilities of finding a particle in various states. It allows for the description of a system's evolution over time, considering the contributions of all possible states. It predicts discrete energy states, as observed in atoms and molecules, thus providing a theoretical basis for the understanding of atomic structure and spectral lines. Thus, its solutions yield critical insights into the nature of matter at the atomic and molecular levels [32].

The Schrödinger Equation can be written in two forms (time dependent and time independent). The time dependent equation describes the evolution of a quantum system over time. It is given by

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H} \Psi(\mathbf{r}, t) \quad (2.1)$$

Where:

- $\Psi(\mathbf{r}, t)$ is the wavefunction, a complex function that contains all the information about the quantum state of the system.
- $\hbar$ is the reduced Planck's constant, defined as $\hbar = \frac{h}{2\pi}$.

- $\hat{H}$ is the Hamiltonian operator, representing the total energy of the system, including both kinetic and potential energies.

In case the potential energy does not depend on time, the equation changes to a time-independent one and is given by

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2.2)$$

Where:

- E is the total energy eigenvalue associated with the wavefunction $\Psi(\mathbf{r})$.

Schrödinger equation can easily be solved for a system of few atoms but in case of a many-body system, there are multiple interacting electrons which increases the number of variables as well as complicates the Hamiltonians. Further exchange effects become significant in such systems and the potential energy spread is a combination of multiple types of interactions (ionic, covalent, Van der Waals, etc.), which makes the equations highly non linear and difficult to solve. Moreover, complex materials often exist in non ideal conditions subjected to external electrical or magnetic fields and also possess disorders. These factors introduce additional complications in accurately solving the Schrödinger equation. The computational resources required for solving the Schrödinger equation for complex systems scale exponentially with the number of electrons. This necessitates the development of advanced computational methods and approximations to analyse and predict the behaviour of complex materials, in short DFT.

2.5 Core principles of DFT

DFT focuses on the electron density $\rho(r)$ rather than on the many-electron wavefunction Ψ (Fig. 2.7). This simplifies the problem since $\rho(r)$ depends only on three spatial variables, regardless of the number of electrons in the system. Effectively, it includes the average effects of electron-electron interactions, which is often sufficient for many practical applications.

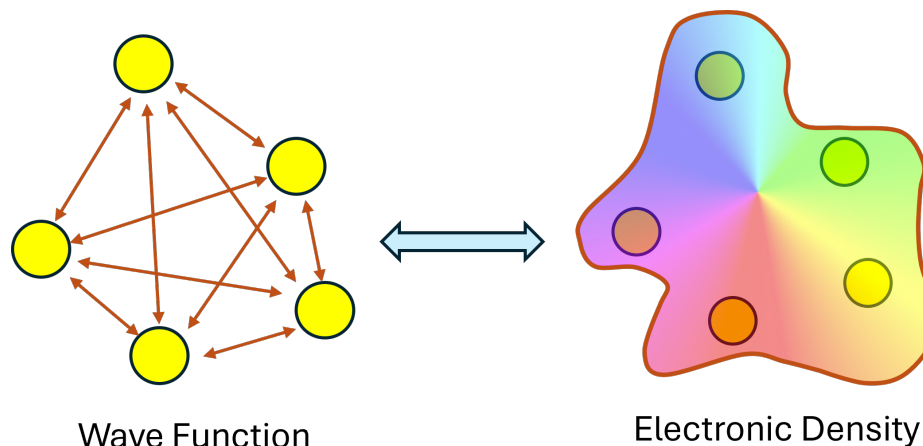


Fig. 2.7 Simplification of Schrödinger equation from wave functions to electronic densities in DFT.

The Hohenberg-Kohn (HK) theorems, established in 1964 by Pierre Hohenberg and Walter Kohn, are the foundation of Density Functional Theory (DFT) [33, 34]. These theorems shifted the focus from the many-body wavefunction to the electron density. The theorems are as follows:

- **First theorem:** The external potential (and hence the total energy) of a many-electron system is a unique functional of the electron density $\rho(\mathbf{r})$. This implies that knowing the electron density is equivalent to knowing the full wavefunction.
- **Second theorem:** The ground-state energy can be obtained by minimising the functional of the electron density, $E[\rho]$, where the true ground-state density gives the minimum energy.

These theorems demonstrate that the ground-state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates, greatly simplifying the many-body problem.

The Kohn-Sham (KS) equations rely on the idea that the exact ground-state electron density $\rho(\mathbf{r})$ of a system of interacting electrons can be represented by the electron density of a system of non-interacting electrons moving in an effective potential $V_{\text{eff}}(\mathbf{r})$. The KS equations are a set of self-consistent equations that describe this non-interacting system. For

each electron, the KS equation takes the form of a one-electron Schrödinger-like equation:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.3)$$

where:

- $\psi_i(\mathbf{r})$ are the KS orbitals (one-electron wavefunctions).
- ε_i are the orbital energies.
- $V_{\text{eff}}(\mathbf{r})$ is the effective potential, defined as:

$$V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_H(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}).$$

- **External Potential** $V_{\text{ext}}(\mathbf{r})$: This is the potential due to atomic nuclei or any other external field acting on the electrons.
- **Hartree Potential** $V_H(\mathbf{r})$: This term describes the classical electrostatic interaction between electrons. It is calculated from the electron density:

$$V_H(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r'.$$

The Hartree potential accounts for the repulsion between electrons, treating them as classical point charges.

- **Exchange-Correlation Potential** $V_{\text{xc}}(\mathbf{r})$: It includes the exchange effects arising from the Pauli exclusion principle, where electrons with the same spin avoid each other and the correlation effects which arise from the correlated motion of electrons due to their mutual repulsion. It is approximated using models like the Local Density Approximation (LDA), Generalised Gradient Approximation (GGA) or Perdew–Burke–Ernzerhof (PBE) functional.

The expression of the total exchange-correlation can be expressed as

$$E_{\text{xc}}[\rho] = E_{\text{x}}[\rho] + E_{\text{c}}[\rho]$$

Where $E_x[\rho]$ is the exchange energy functional corresponding to the energy transfer between electrons of the same spin and $E_c[\rho]$ corresponds to the correlation energy between opposite spin electrons.

2.6 Flow of steps in DFT logic calculation

Using exchange-correlation (XC) functionals and treating the system as non-interacting, one can solve the KS equations. The resulting solutions, referred to as KS orbitals, must be obtained in a self-consistent manner. The KS orbitals, electron densities, and the Hamiltonian are interrelated, and all these elements must be considered to achieve convergence.

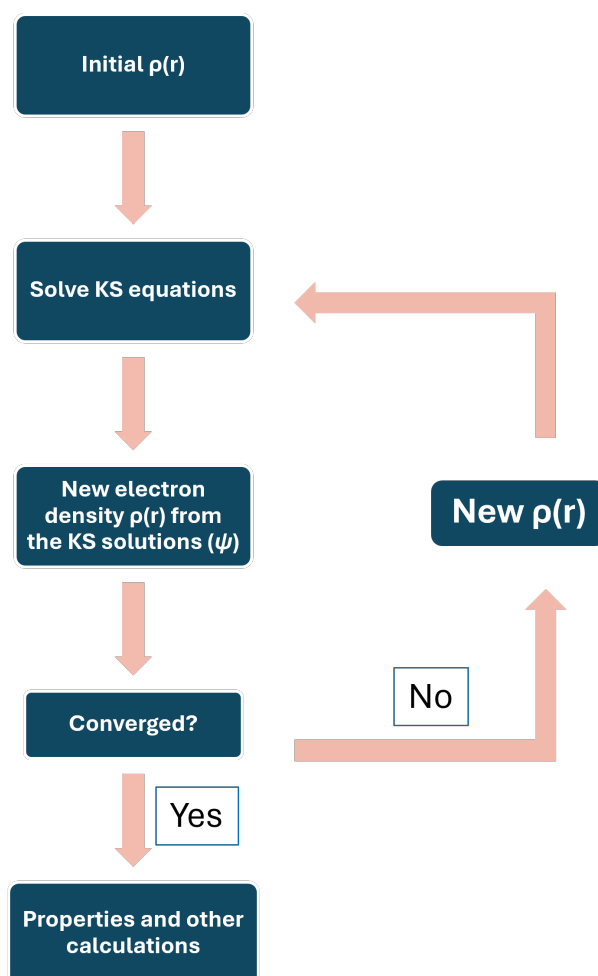


Fig. 2.8 Scheme representing the flow of DFT algorithm.

The convergence scheme has been shown in Fig. 2.8. The algorithm begins by choosing an initial guess for the electron density $\rho(r)$. The electron density is used to solve the KS equations iteratively to find the wavefunction ψ . Using this new ψ , the $\rho(r)$ is updated. The updated $\rho(r)$ is compared to the previous $\rho(r)$. If the difference between the new and old densities is below a pre-defined threshold, the solution is considered converged. If convergence has not been achieved, a new density is generated by mixing the old and new densities, a method known as density mixing. The algorithm then returns to step 2 and the cycle repeats till the convergence is met. Once the convergence is achieved, the required properties and other calculations can be performed as needed.

2.7 EELS and ELNES from DFT

The calculation of EELS and ELNES spectra using DFT typically involves three main steps:

1. **Density of States (DOS) calculation:** The first step in the process involves calculating the DOS by solving the KS equations within DFT. This yields the energy levels (eigenvalues) and electronic wave functions, which are then used to construct the DOS. The total DOS represents the number of available electronic states at each energy level, while the partial DOS (PDOS) provides insights into the orbital and atomic contributions.
2. **Optical properties calculation:** Using the DOS, DFT calculates optical properties such as the dielectric function, $\epsilon(\omega)$, which describes the material's response to electric fields. The imaginary part of the dielectric function, derived from interband transitions, is particularly important as it represents the material's absorptive properties and is foundational in modelling energy loss.
3. **EELS and ELNES spectrum generation:** The final step utilises the dielectric function and DOS to simulate the EELS and ELNES spectra. In low loss EELS, the energy loss function, $\text{Im}\left(-\frac{1}{\epsilon(\omega)}\right)$, is derived from the dielectric function, capturing plasmonic and

interband excitations. For ELNES, transitions from core levels to unoccupied states are calculated from PDOS features, reflecting the local bonding and electronic structure in the near-edge region.

2.7.1 DOS and PDOS calculation

The eigenvalues ϵ_i represent the energies of the electronic states, and the wave functions $\psi_i(\mathbf{r})$ describe the distribution of electrons. In DFT, we can obtain this by solving the KS equation as mentioned in equation 2.3.

The density of states (DOS) is calculated from the eigenvalues ϵ_i by summing over all energy levels:

$$D(E) = \sum_i \delta(E - \epsilon_i), \quad (2.4)$$

where $D(E)$ is the total DOS at energy E , and $\delta(E - \epsilon_i)$ is the Dirac delta function, which counts the states at each eigenvalue. In practical implementations, a small broadening factor (usually Gaussian or Lorentzian) is applied to smooth the DOS curve, making it easier to interpret.

For PDOS, which provides insights into the contributions of specific atomic orbitals or elements, the DOS is projected onto these specific atomic states (e.g., s , p , and d -orbitals). The PDOS can reveal orbital-specific features that are essential in interpreting bonding and spectral characteristics [35].

2.7.2 Optical properties calculation

Once the DOS is obtained, the optical properties of the material can be calculated. These properties are foundational for simulating EELS spectra, as EELS measures the energy lost by electrons due to interactions with the electronic structure of the material.

The dielectric function,

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega),$$

describes the material's response to an oscillating electric field. For EELS, the imaginary part $\varepsilon_2(\omega)$ is particularly important, as it represents the absorption within the material and reflects the material's electronic structure.

The imaginary part of the dielectric function is given by:

$$\varepsilon_2(\omega) = \frac{8\pi^2 e^2}{\Omega} \sum_k \sum_{i,j} \frac{|\langle \psi_j(k) | \mathbf{e} \cdot \mathbf{r} | \psi_i(k) \rangle|^2}{(E_j(k) - E_i(k))^2} \delta(\hbar\omega - (E_j(k) - E_i(k))),$$

where:

- $\mathbf{e}$ is the polarization vector,
- $E_i(k)$ and $E_j(k)$ are the initial and final state energies,
- $\delta(\hbar\omega - (E_j(k) - E_i(k)))$ represents the energy conservation condition, ensuring transitions occur only at the specified photon energy $\hbar\omega$ [36].

This equation considers all possible transitions between occupied and unoccupied states, weighted by the transition matrix elements and the DOS at each energy. The real part $\varepsilon_1(\omega)$ of the dielectric function can be calculated from $\varepsilon_2(\omega)$ using the Kramers-Kronig relations, which link the real and imaginary components.

The energy loss function (ELF) for simulating low loss EELS spectra, is given by:

$$\text{Im} \left(-\frac{1}{\varepsilon(\omega)} \right) = \frac{\varepsilon_2^2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} \text{Im}(-\varepsilon(\omega))$$

This function represents the energy lost by electrons as they traverse the material and undergo excitations. Peaks in this function indicate plasmon resonances and interband transitions, providing insights into both the bulk and surface plasmonic properties of the material [37].

2.7.3 EELS and ELNES spectrum generation

With the DOS and optical properties calculated, the final step is generating the EELS and ELNES spectra. EELS focuses on the collective and single-electron excitations within

the material, while ELNES examines fine structure near ionisation edges, reflecting local bonding and coordination environments.

ELNES focuses on the fine structure observed in the energy-loss spectrum. It is sensitive to the local electronic structure and the chemical environment of specific atoms within a material. In ELNES, electrons are excited from core levels (e.g., 1s, 2p) to unoccupied states above the Fermi level. The characteristics of these transitions depend heavily on the local bonding environment and the nature of the unoccupied states. Its spectrum exhibits sharp features, often described as peaks or shoulders, which correspond to specific electronic transitions. These features are highly sensitive to the symmetry and hybridisation of the bonding orbitals, providing detailed information about the local coordination of atoms. The intensity of the ELNES spectrum can be expressed as:

$$I(\omega) = \sum_{i,f} |\langle \psi_f | \mathbf{q} \cdot \mathbf{r} | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

where ψ_i and ψ_f are the initial and final state wave functions, $\mathbf{q}$ is the momentum transfer vector, and $\delta(E_f - E_i - \hbar\omega)$ ensures energy conservation for the transitions. The spectral features depend on the local density of states (LDOS) near the Fermi level, highlighting how local environments affect electronic transitions.

To illustrate the use of the simulations to interpret experimental changes in ELNES, we provide an analysis for the identification of lithiated and delithiated regions in lithium iron phosphate (LiFePO_4 , henceforward referred as LFP) cathodes from a solid oxide fuel cell, using both Li K edge and Fe $L_{2,3}$ and $M_{2,3}$ edges. The samples were provided by the team of Dr. Alejandro Morata Garcia from the Nanoionics and Fuel Cells department of the Catalonia Institute for Energy Research (IREC). These materials are typically used in solid state battery industries [38]. The bilayer structure consisting of LFP and $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP) thin films was deposited on silicon chips coated with platinum. Following deposition, the samples underwent rapid thermal processing (RTP) at 800°C for 60 seconds under an argon atmosphere with a ramp rate of 10°C/s to achieve crystallinity and interfacial adhesion.

In the primary analysis of LFP cathodes, by applying clustering methods [39] on the experimental EELS data as obtained from the spectrum image shown in Fig. 2.9(a), two

distinct regions emerged, labelled as bulk and defect regions, as shown in Fig. 2.9(b). These two regions presented differences in both, low loss (Fig. 2.10(c)) and high energy loss spectra (Fig. 2.9(c)). A hypothesis was made that the defective regions might remain delithiated after several charge cycles. To account for the presence and/or absence of Li, ELNES of LiFePO_4 and FePO_4 were simulated as shown in Fig. 2.9(d). In LiFePO_4 and FePO_4 , Fe has an oxidation state of Fe(II) and Fe(III) respectively. Upon observing the fine structure of Fe (by comparing Fig. 2.9(c) and 2.9(d)), it was possible to note distinct features that can be linked to the simulated ELNES. The bulk region, with maxima at lower energies and thinner peaks correspond well to the simulated LFP with Fe(II). Conversely, the defective region is similar to Fe(III) owing to maxima appearing at higher energies and having thicker peaks. This points towards a fully lithiated bulk LFP and delithiated defects.

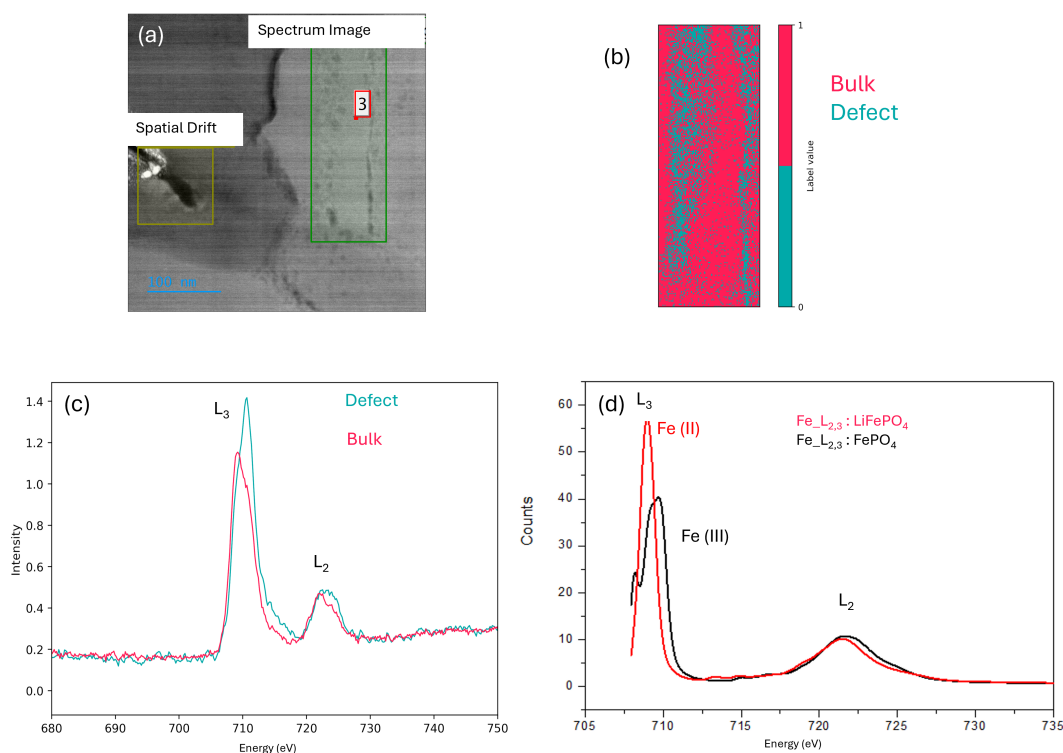


Fig. 2.9 Comparison of Fe $L_{2,3}$ in bulk and defective regions of LFP cathodes using ELNES simulations. (a) EELS spectrum image (b) Experimental EELS region, with areas of the bulk and defect, (c) Experimental EELS averaged spectrum, (d) Simulated ELNES of Fe of two different phases.

Low loss EELS experimental and simulation results are shown in Fig. 2.10. In the low loss region, a small bump can be observed after the Fe $M_{2,3}$ edge only present in the areas without defects (bulk) (Fig. 2.10(c)). This is not clearly observed in the Fe $M_{2,3}$ simulations (Fig. 2.10(d)) but corresponds well to the simulated Li K edge energy (Fig. 2.10(e)) (note the small intensity of the Li transition when compared with the Fe). This confirms that the defective area also lacks Li which is in good correspondence to the change in Fe oxidation state observed in the core-loss region.

Therefore, ELNES simulation has been the key in understanding the experimental data. By employing these techniques in tandem with other DFT calculations, we can aim to achieve a comprehensive understanding of material properties at the atomic scale.

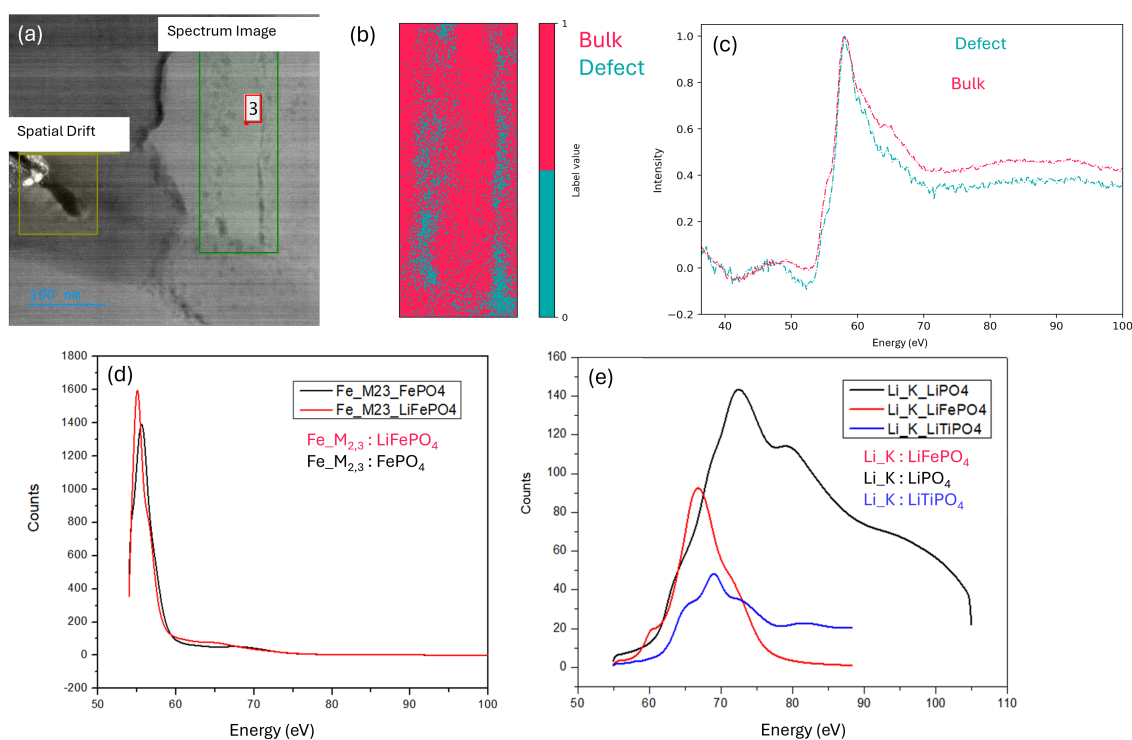


Fig. 2.10 Low loss EELS comparison of bulk and defect regions of LFP cathodes using ELNES simulations (a) EELS spectrum image (b) Experimental EELS region, with areas of the bulk and defect, (c) Experimental EELS averaged spectrum, (d) Simulated $M_{2,3}$ Fe edge of two different phases, (e) Simulated low loss EELS of Li K edge in three different phases.

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Chapter 3

Material engineering in hafnia-based RRAMs: linking structural phases, stoichiometry and dielectric function

This chapter delves into the structural and dielectric properties of r -HfO_{1.7}-based Resistive Random Access Memory (RRAM), an emerging non-volatile memory technology. By investigating the phase transitions and stoichiometric variations intentionally induced by controlled environmental exposure, this work provides insights into how these structural changes affect the dielectric properties, which critically influence device performance.

Combining simulations with experimental techniques, we reveal how oxygen vacancies and phase transformations contribute to the unique behaviour of r -HfO_{1.7}. These findings emphasise the importance of material engineering in optimising device performance and pave the way for further advancements in RRAM technology.

3.1 HfO₂ based RRAM: importance and application

Hafnium Dioxide (HfO₂), also known as hafnia, is a material of significant technological importance due to its unique properties, particularly for future microelectronic applications [1]. It possesses a high dielectric constant due to the large permittivity and wide band gap [2–5], making it a crucial material in the semiconductor industry, particularly in transistors. Its exceptional neutron absorption capabilities make it an ideal material for control rods in nuclear reactors as well [6]. Additionally, its high-temperature stability makes it an excellent candidate for thermal barrier coatings in turbine engines [7].

Beyond these applications, HfO₂ also plays a pivotal role in the development of next-generation memory technologies, particularly in resistive random access memory (RRAM) devices. These HfO₂-based RRAM devices are increasingly used in Internet of Things applications owing to their low power consumption, scalability, non volatility, easier fabrication, fast switching speeds and long data retention time [8–11]. They perform well in high-temperature environments and are suitable for systems like vehicle-to-vehicle (V2V) communication, industrial sensors, wearable devices, and smart-home technologies [12]. Their seamless integration with CMOS technology makes them ideal for embedded memory solutions. Moreover, RRAM devices are valuable for computing tasks due to their low power consumption, low operating voltages, and their potential to meet the requirements of emerging embedded memory applications by efficiently integrating memory and processing functions. [13]. Their durability and flexibility ensure consistent performance even under mechanical stress, making them particularly suited for wearable electronics [14]. Furthermore, HfO₂-based RRAM devices are being actively explored for neuromorphic computing, where they mimic synaptic functions, enabling the development of artificial neural networks and spiking neural networks [15].

3.2 Role of oxygen vacancies in hafnia-based RRAM

A key factor influencing the performance of hafnia-based RRAM is the presence and distribution of oxygen vacancies. Oxygen vacancies are critical for the formation and

stability of conductive filaments. The distribution and concentration of these vacancies significantly affect the resistive switching behaviour and device performance [14, 16–19]. A basic RRAM design consists of a simple metal-insulator-metal structure, with the HfO_2 layer sandwiched between two metal electrodes as shown in Fig. 3.1. An asymmetric distribution of oxygen vacancies at the $\text{HfO}_2/\text{TiO}_2$ interface enhances the performance of flexible RRAM devices, contributing to high durability and mechanical flexibility [14]. Modulating the oxygen vacancy profile through techniques, such as adjusting oxidant pulse time during atomic layer deposition, can alter the resistive switching behaviour, switching mechanisms, and current transport mechanisms in such RRAM devices [16, 20]. It has also been proven that engineering the oxygen stoichiometry in HfO_x based devices can stabilise filament formation and enable multiple switching modes, contributing to improved device performance and reliability [21]. The structural integrity and chemical composition of the layers in RRAMs are crucial as they dictate the dielectric properties, which directly influence key performance metrics such as switching speed, endurance, retention, and energy efficiency. These dielectric properties play a vital role in determining how the material stores and dissipates electrical energy, which is essential for consistent filament formation and disruption. If the dielectric material has unsuitable properties, it can lead to challenges such as leakage currents, switching variability, or even premature device failure. Moreover, the uniformity of the dielectric layers significantly impacts the filament formation process, ultimately affecting the reliability and scalability of RRAM devices.

In this study, we start by understanding two HfO_x based device's fabrication techniques and experimental readings, followed by simulating in DFT the oxygen vacancies to reveal their effects on the dielectric function.

3.3 Fabrication of RRAM

The samples were prepared by the Advanced Electron Microscopy Group at Technische Universitat Darmstadt. Two types of HfO_x based devices were fabricated, namely monoclinic (m- HfO_2) and rhombohedral (r- $\text{HfO}_{1.7}$) as shown in Fig. 3.1.

For the deposition technique, all the thin films were grown using a Molecular Beam Epitaxy (MBE) system with a base pressure ranging from 10^{-8} to 10^{-9} mbar. Device fabrication was carried out on C-cut sapphire substrates. Hafnium layers were deposited using metallic hafnium and a controlled flux of oxygen radicals, generated at a RF plasma power of 200 W, with the substrate maintained at a temperature of 320 °C.

Monoclinic hafnia was grown at a hafnium deposition rate of 0.1 Å/s with an oxygen flux of 0.18 sccm and the rhombohedral hafnia was deposited at a hafnium rate of 0.9 Å/s, with a lower oxygen flux of 0.1 sccm, while being exposed to air. Titanium nitride (TiN) layers were deposited at a substrate temperature of 800 °C using a Ti source with an evaporation rate of 0.2 Å/s and an RF plasma power of 340 W. Substrate temperature was monitored and calibrated using a thermocouple.

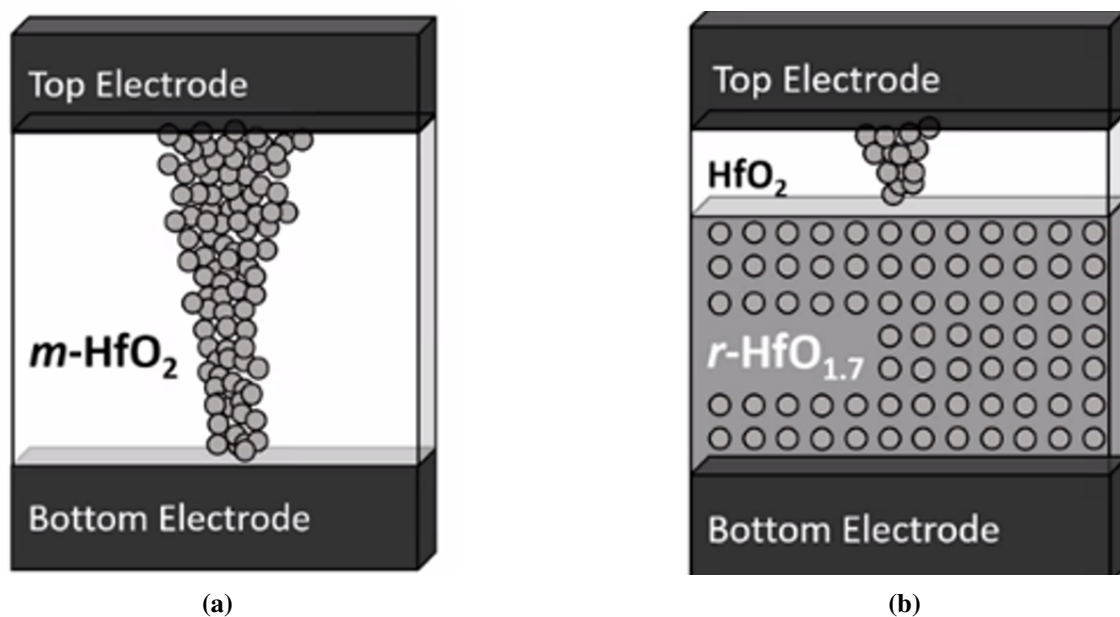


Fig. 3.1 HfO_x device layout. (a) monoclinic (m-HfO₂), (b) rhombohedral (r-HfO_{1.7}). For both devices, bottom electrode is TiN and top electrode is Pt. The extent of the potential formation of a conductive filament in the hafnia is also represented.

3.4 Preliminary characterisation

For each of the devices, cross-sectional TEM lamellas were prepared with a JEOL 4600F Focused Ion Beam (FIB) instrument. The lamellas were investigated with the JEOL-ARM200F electron microscope operated at 200 kV.

In High Angle Annular Dark Field (HAADF) images, the image intensity is directly proportional to Z raised to a power α , typically ranging between 1.4 - 2 [22, 23], heavier elements, with higher atomic numbers, give rise to higher intensities. On the contrary, Annular Bright Field (ABF) images can reveal light element details that are not visible in HAADF images [24]. The HAADF and ABF images of m-HfO₂ and r-HfO_{1.7} are shown in Fig. 3.2. Both devices exhibit distinct structural features, including clearly identifiable layers of titanium nitride (TiN), a hafnia layer, and platinum. However, a notable difference arises in the case of r-HfO_{1.7}. In this material, the hafnia layer appears to be separated into two distinct regions with varying intensities, one exhibiting a higher intensity and the other a lower one. Specifically, in Fig. 3.2(b) and Fig. 3.2(d), the image of r-HfO_{1.7} provides a clear distinction between the two sub-layers, a predecessor layer (r-HfO_x) and a top layer, here referred to as t-HfO_{x+y} within the hafnia region, showcasing the contrast variation related to differing oxygen content, since in the case of r-HfO_{1.7}, the material was exposed to air, probably leading to partial oxygenation. In contrast, m-HfO₂ was prepared and maintained under vacuum conditions, which prevented this segregation and maintained a uniform oxygen distribution across the layer, as confirmed by the uniform contrast observed in its ABF image (Fig. 3.2(a)).

For further validation of the STEM results, the EDS measurements for m-HfO₂ and r-HfO_{1.7} are shown in Fig. 3.3. For the m-HfO₂ sample, the atomic percentage composition reveals a straightforward and well-defined layered structure with three distinct regions: a TiN layer at the bottom, characterised by strong titanium and nitrogen signals; a middle layer of m-HfO₂, exhibiting a consistent ratio of hafnium to oxygen, indicative of the stoichiometric monoclinic phase; and a top layer of platinum. This composition aligns precisely with the expected structure of the m-HfO₂ sample. The clarity of these results provides a solid foundation for comparison with the more complex r-HfO_{1.7} sample.

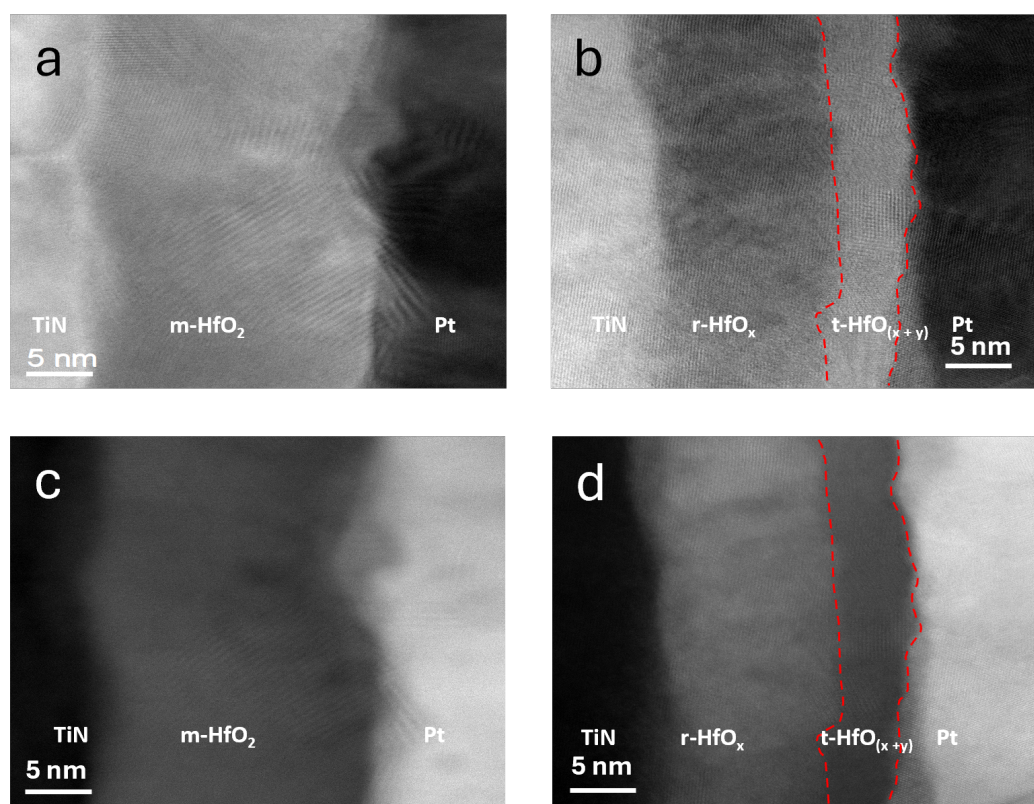


Fig. 3.2 ABF (a, b) and HAADF (c, d) of m-HfO₂ (a, c) and r-HfO_{1.7} (b, d). r-HfO_{1.7} depicts two oxide layers, one being richer in oxygen t-HfO_{x+y} than the other r-HfO_x.

In contrast, the EDS analysis of the r-HfO_{1.7} sample unveils a different compositional profile. While the bottom TiN layer and top Pt layer remain clearly identifiable, the hafnium oxide region exhibits a notable oxygen gradient. Near the TiN interface, a relatively stable Hf/O ratio is observed, likely corresponding to the r-HfO_{1.7} phase. However, as the analysis progresses away from this interface, a significant change in the Hf/O ratio becomes apparent. The Hf signal decreases markedly, while the O signal shows only a slight reduction, indicating the presence of a more oxygen-rich phase, tentatively labelled as t-HfO_{x+y}. This compositional variation suggests a possible phase transition from r-HfO_{1.7} to a higher oxygenated layer. The EDS results, therefore, provide confirmation of the presence of a higher oxygenated layer in r-HfO_{1.7}, which is consistent with HAADF and ABF results.

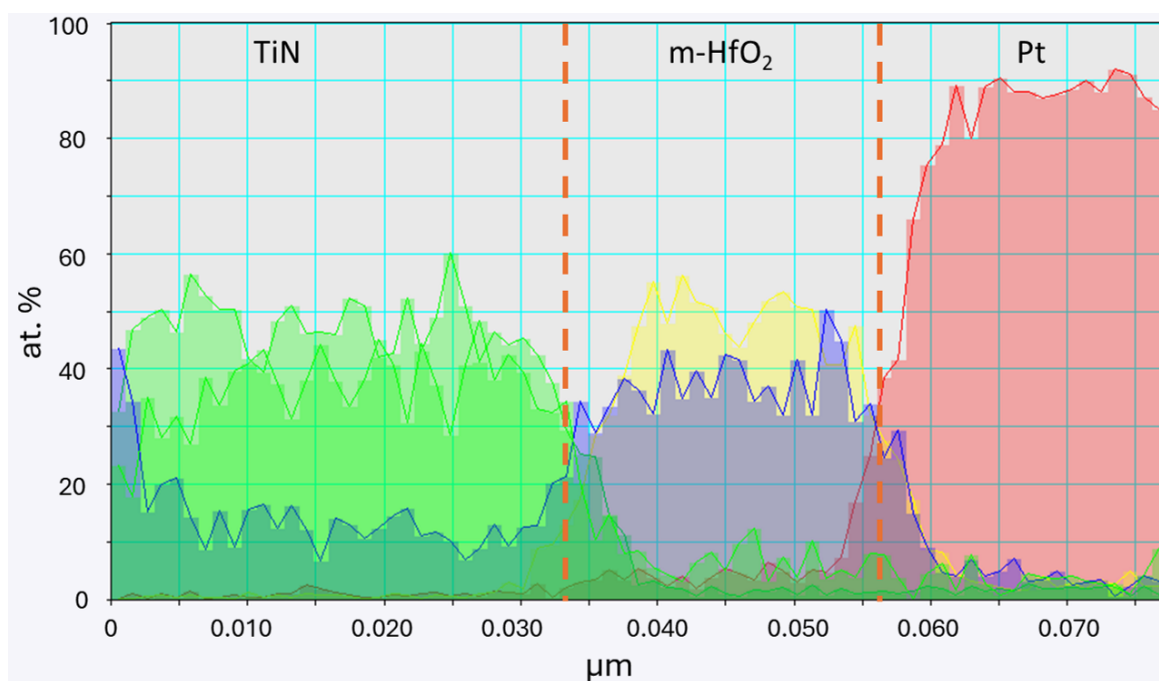
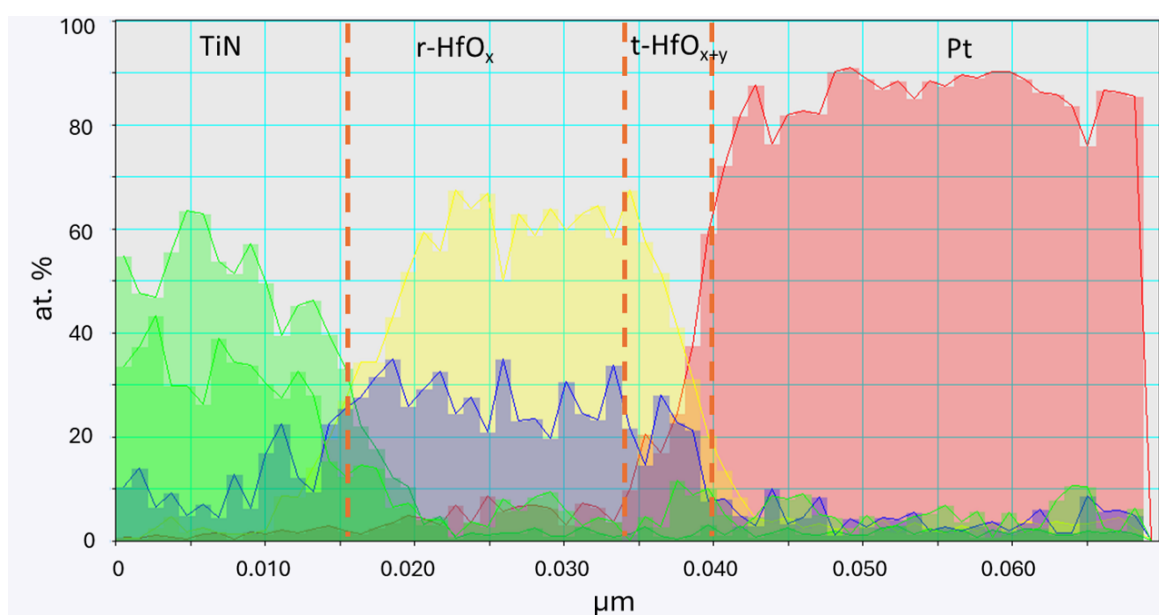
(a) m-HfO₂(b) r-HfO_{1.7}

Fig. 3.3 Comparison of quantified EDS data for (a) m-HfO₂ and (b) r-HfO_{1.7} depicting the changes in ratio of Hf to O, particularly at the interface of HfO_x/Pt.

As the oxygenated layer arises only in the case of rhombohedral sample and no changes are observed in the monoclinic sample, our interest shifts to study the structural changes that are brought by the oxidation at the rhombohedral sample only.

Fast Fourier Transform (FFT) analysis was performed on the HRTEM image on the $r\text{-HfO}_x$ and $t\text{-HfO}_{x+y}$ regions as shown in Fig. 3.4. The observations indicate that the distances and positions of the reflections corresponding to the $r\text{-HfO}_x$ hafnia layer (blue region) match those of the rhombohedral phase (R3m), while the $t\text{-HfO}_{x+y}$ hafnia layer (green region) match those of the monoclinic phase (P21/c), indicating that a transformation of phase happens upon the addition of oxygen. This finding points towards a structural change from rhombohedral to monoclinic upon the oxidation of the hafnia layer and opens the door for the verification of such findings via simulation studies.

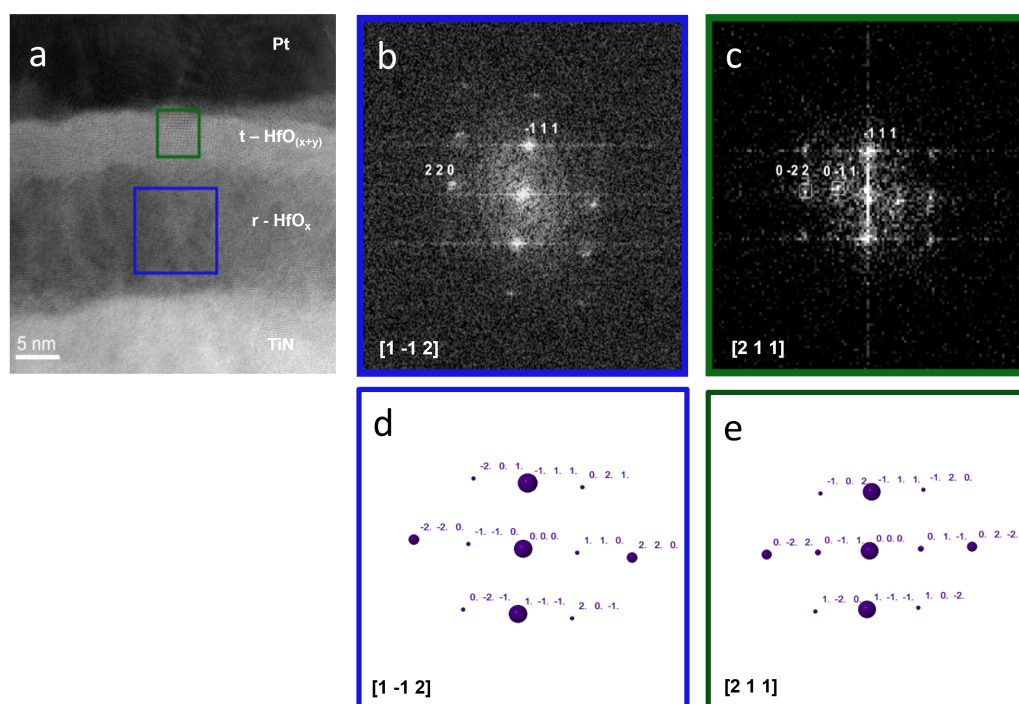


Fig. 3.4 (a) HRTEM image for the rhombohedral hafnia sample and the FFT images for the $r\text{-HfO}_x$ and $t\text{-HfO}_{x+y}$ layers: (b) FFT image with zone axis $[1 \bar{1} 2]$ of R3m symmetry, (c) FFT image with zone axis $[2 1 1]$ corresponding to the P21/c symmetry, (d) and (e) are the theoretical diffraction patterns of (b) and (c) respectively.

3.5 EELS analysis

The existence of dissimilar oxygenated layers suggests that the dielectric function of the device should change as per the structure of the concerned layer. Therefore, to study the dielectric function we chose two areas of equal dimensions on the r-HfO_x and t-HfO_{x+y} as shown in Fig. 3.5. For comparison purpose, an equal area was also chosen on the m-HfO₂ sample.

The complex dielectric function (CDF), comprising the real part (ϵ_1) and the imaginary part (ϵ_2), was computed for each area using Kramers-Kronig (KK) analysis of the EELS data, following the algorithm developed by Eljarrat [25]. Figure 3.6 illustrates the calculated CDFs, with vertical lines indicating the energy at which the real and imaginary components intersect. This intersection, a characteristic feature of the CDF, occurs at 14.7 eV for m-HfO₂ sample. For the r-HfO_{1.7} sample, it is at 11 eV for r-HfO_x layer, whereas for t-HfO_{x+y}, it is shifted to 14.2 eV. This observed shift in t-HfO_{x+y} suggests a modification of the dielectric properties due to increased oxygen concentration. Additionally, the intersection energy for t-HfO_{x+y} closely matches that of m-HfO₂. For better visualisation, separate comparisons of only the real and imaginary parts are shown in Fig. 3.7. The shape of both ϵ_1 and ϵ_2 for t-HfO_{x+y} and m-HfO₂ are very similar and are different from that of r-HfO_x. These results confirm that exposure to oxygen has led to a modified layer. To further evaluate and affirm our findings, simulations were performed as explained in the next section.

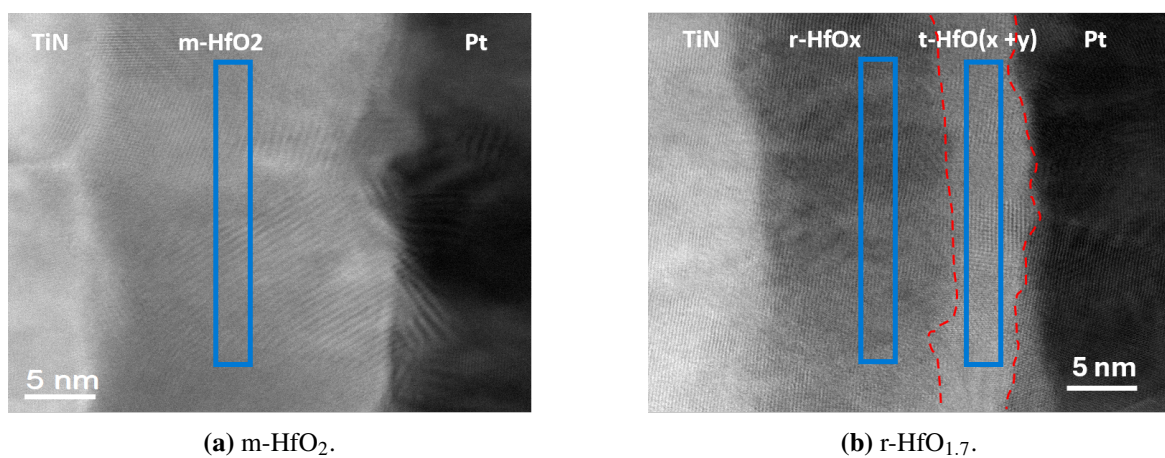
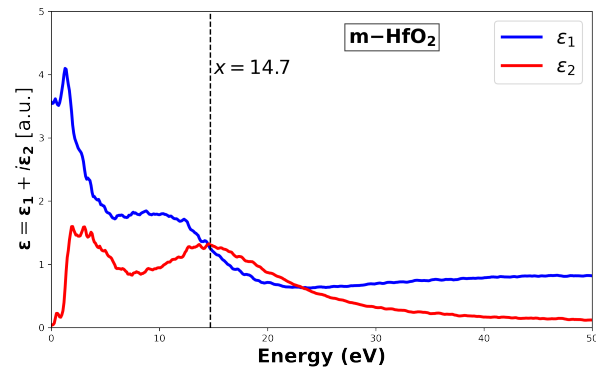
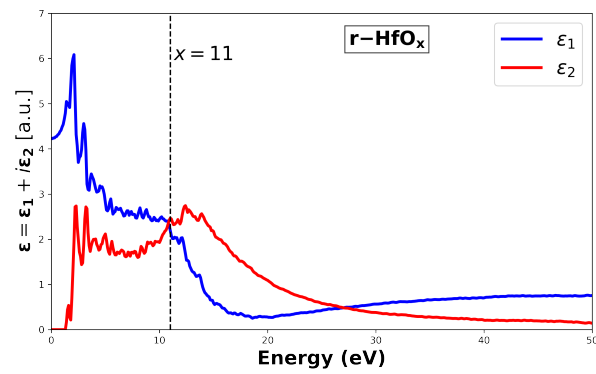


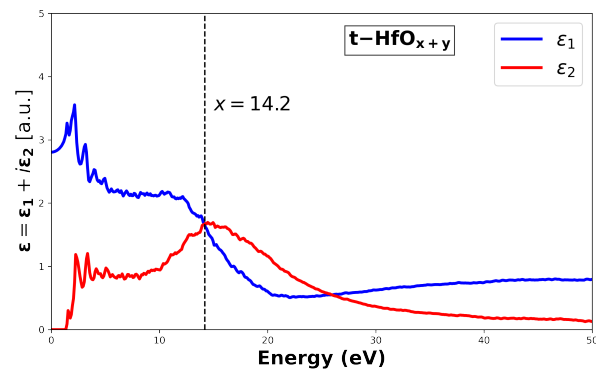
Fig. 3.5 Selected area (in blue box) for KK analysis: (a) m-HfO₂, and (b) r-HfO_{1.7}.



(a)

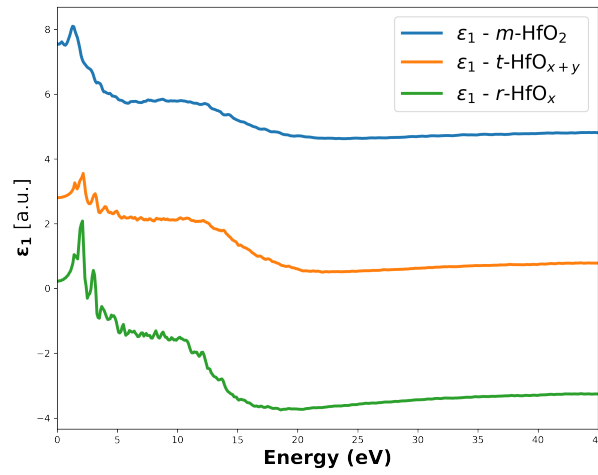


(b)

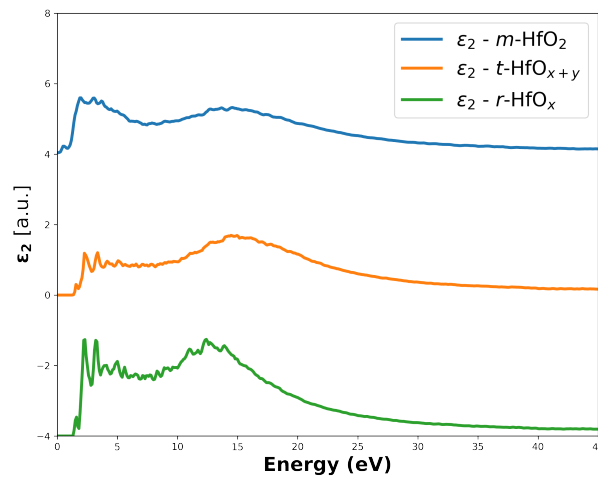


(c)

Fig. 3.6 Dielectric function of (a) m-HfO₂, (b) r-HfO_x, and (c) t-HfO_{x+y}, depicting that the characteristics of oxygenated hafnia layer are in close resemblance to that of m-HfO₂.



(a)



(b)

Fig. 3.7 Comparison of (a) real, and (b) imaginary parts of CDF for $m\text{-HfO}_2$, $r\text{-HfO}_x$ and $t\text{-HfO}_{x+y}$.

3.6 Dielectric function simulation

DFT simulations help in understanding the electronic and structural properties of hafnia and its derivatives. By providing atomistic insights, DFT enables the calculation of the CDF, offering a direct comparison with experimental results such as EELS-derived dielectric functions. In the case of $r\text{-HfO}_x$ and $t\text{-HfO}_{x+y}$, DFT simulations can elucidate the impact

of varying oxygen stoichiometry on the CDF by predicting how oxidation and structural changes influence the dielectric properties.

3.6.1 Structural modelling and oxygen vacancies

For the simulations, the two structural configurations confirmed in the samples, m-HfO₂ and r-HfO_{1.75}, were considered, as illustrated in Fig. 3.8. The m-HfO₂ structure represents a stoichiometric form of hafnia, which is the thermodynamically stable phase at ambient conditions. In contrast, the r-HfO_{1.75} structure was derived by systematically removing one of the eight symmetrically equivalent oxygen atoms from the cubic HfO₂ phase, followed by a full geometric relaxation to stabilise the resulting rhombohedral symmetry, yielding the r-HfO_{1.75} [26].

The unit cell parameters after relaxation, for both structures are presented in Table 3.1. The m-HfO₂ phase exhibits an asymmetric unit cell with distinct lattice parameters and angles characteristic of a monoclinic structure. Conversely, the r-HfO_{1.75} phase is defined by equal lattice parameters and angular distortions typical of a rhombohedral geometry.

To ensure computational feasibility while maintaining physical accuracy, the unit cells were expanded into supercells of $2 \times 1 \times 1$ dimensions as shown in Fig. 3.9. This transformation provides a larger simulation domain, essential for accurately modelling the electronic and dielectric properties while minimising the boundary effects that might arise in smaller unit cells. DFT simulations were subsequently performed on these supercells to calculate the dielectric function for both m-HfO₂ and r-HfO_{1.75}.

Hafnia is widely known for the presence of oxygen vacancies [27–29]. To further enhance the realism of our simulations, we introduced minor vacancies in the supercells. For both the cases at first, only one oxygen was removed from one of the non-symmetrical positions and the results were compared to that of the experimental. Further, two atoms were also removed to check the effects on the dielectric function. Here we report the best obtained results out of the multiple trials that have been performed. It has been found that the removal of one oxygen atom from r-HfO_{1.75} and two atoms from m-HfO₂ as shown in Fig. 3.9 resulted in the closest match, as explained in the following sections.

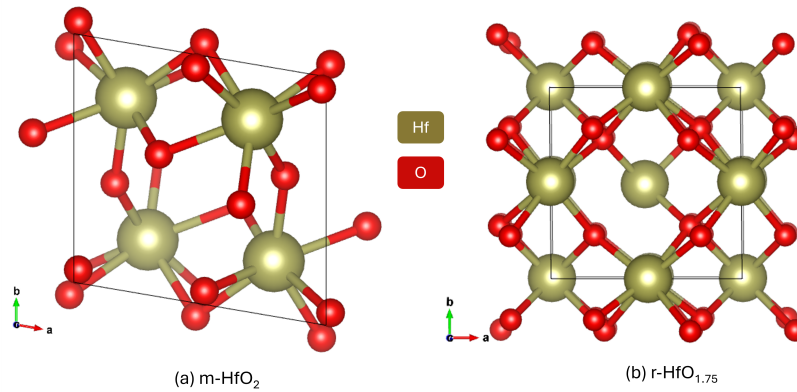


Fig. 3.8 Unit cell structure of (a) m-HfO₂, and (b) r-HfO_{1.75}.

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
m-HfO ₂	5.23498	5.07846	5.16442	90.0000	90.0000	99.6672
r-HfO _{1.75}	5.02028	5.02028	5.02028	90.5356	90.5356	90.5356

Table 3.1 Lattice parameters for the unit cell of (a) m-HfO₂ and (b) r-HfO_{1.75}.

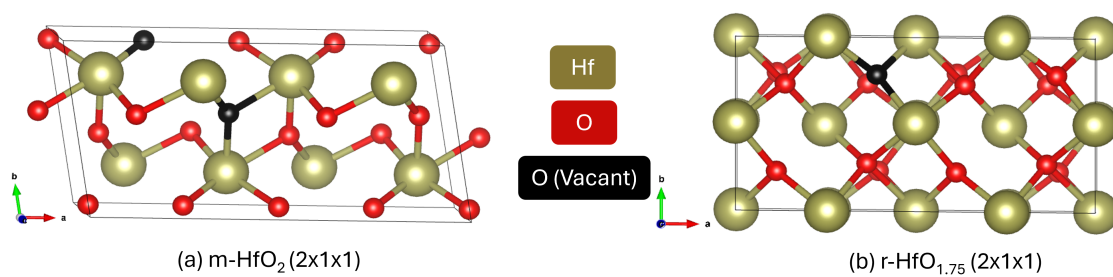


Fig. 3.9 Supercell structure of (a) m-HfO₂, and (b) r-HfO_{1.75} with oxygen vacancies .

3.6.2 Simulation results

For each of the supercells with vacancy configurations, the structures were subjected to geometric relaxation using the Vienna Ab Initio Simulation Package (VASP) [30]. The geometry of the systems was relaxed to minimise the forces on the atoms, ensuring that the structures reached their lowest energy configuration. The Perdew-Burke-Ernzerhof [31] functional was utilised. A plane-wave energy cutoff of 500 eV was chosen. The Brillouin zone was sampled using a Monkhorst-Pack k-point mesh of $10 \times 10 \times 10$. The convergence criteria for the relaxation were set at 10^{-5} eV. Once the relaxed structure was found, the "optics" simulation module was applied by setting the precision to accurate mode and sigma to 0.01 to obtain the dielectric properties of the structure.

The normalised simulation results of the dielectric function for supercells with and without vacancies in $r\text{-HfO}_{1.75}$ and $m\text{-HfO}_2$ are shown in Figs. 3.10 and 3.11, respectively. A significant difference is observed in the 0–5 eV range for all cases. In $r\text{-HfO}_{1.75}$, the dielectric function ϵ_1 for the vacancy-containing supercell exhibits a lower intensity around the energy of 2.5 eV compared to the vacancy-free case, while the intensity ϵ_2 is higher. Similarly, for $m\text{-HfO}_2$, the intensity of ϵ_1 is lower in the vacancy-containing supercell around 6 eV, while ϵ_2 shows a higher intensity around 2.5 eV compared to the vacancy-free case.

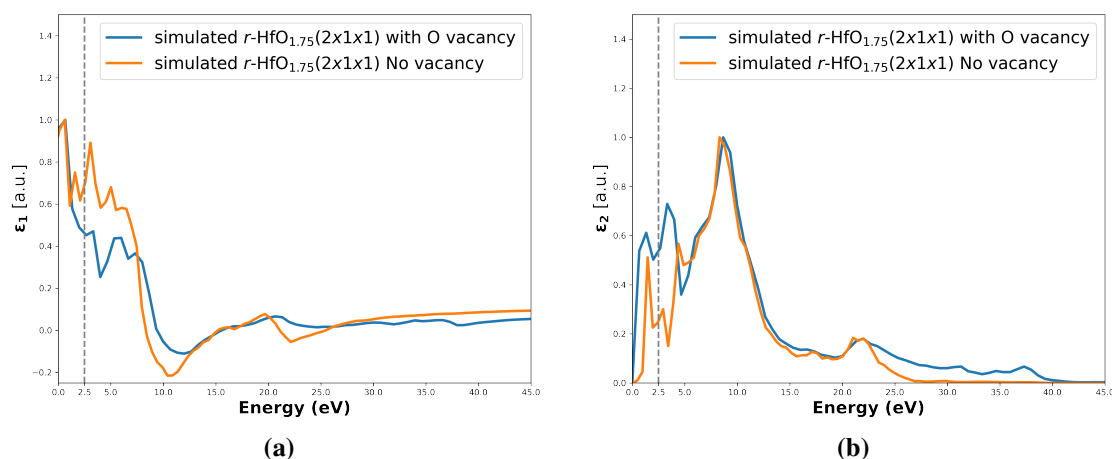


Fig. 3.10 Dielectric function simulation ((a) real, and (b) imaginary) of $r\text{-HfO}_{1.75}$ supercell with and without oxygen vacancy.

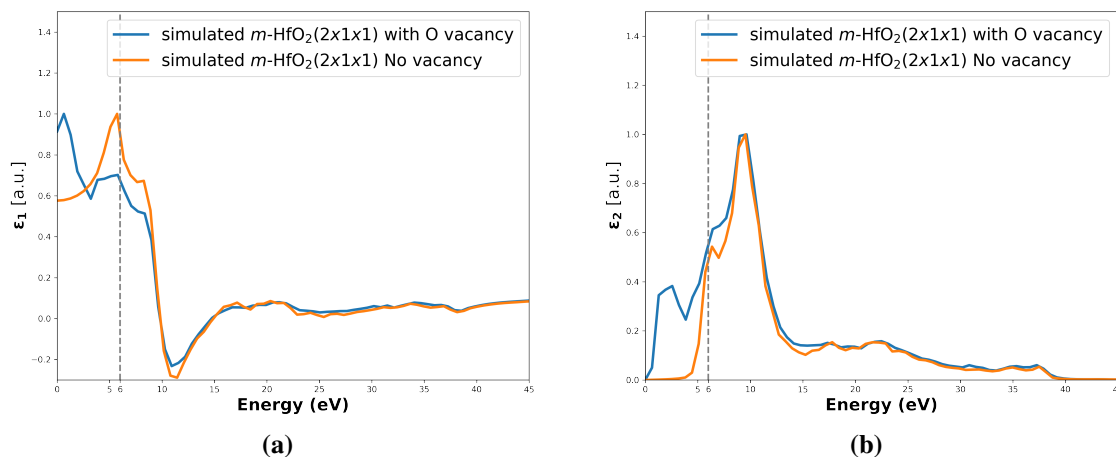


Fig. 3.11 Dielectric function simulation ((a) real, and (b) imaginary) of $m\text{-HfO}_2$ supercell with and without oxygen vacancy.

We performed a comparison of the dielectric function of $r\text{-HfO}_{1.75}$ with $r\text{-HfO}_x$ and $m\text{-HfO}_2$ with $t\text{-HfO}_{x+y}$, as shown in Figs. 3.12 and 3.13, respectively. EELS simulated data in WIEN2K suffers a shift in the energy axis owing to various factors (relativistic calculations, broadening, onset parameters) [32–35]. Therefore, to improve the fit, the simulated plots have been shifted by 3 eV towards low energy. Overall, the simulated dielectric functions match the experimental results across all cases. The results of the simulated dielectric function of $m\text{-HfO}_2$ confirms the experimental finding that the oxygen-rich area in the rhombohedral hafnia layer undergoes a phase transition to a monoclinic phase upon oxidation. However, some minor discrepancies are noticeable, particularly around 10 eV. These differences can be attributed to several factors. First, the sample thickness was approximately 150 nm, as determined by KK calculations. This relatively large thickness could introduce effects such as multiple scattering, which may not be fully captured in the simulations, leading to slight deviations in the spectral data. Second, the exact number and ordering of oxygen vacancies in the system remain difficult to quantify with precision at this stage. Variations in the vacancy concentration and distribution significantly influence the dielectric response.

The simulated dielectric function of $m\text{-HfO}_2$ is the best match for the experimental dielectric function of the $t\text{-HfO}_{(x+y)}$ region, strongly suggesting that the incorporation of oxygen into the rhombohedral lattice during exposure to air induces a local transformation

favouring the formation of a monoclinic structure. This structural change is visually consistent with the ABF and HAADF images (Fig. 3.2(b) and 3.2(d), which show a clear contrast difference and distinct structural arrangement between the rhombohedral $r\text{-HfO}_x$ region and the oxygen-rich $t\text{-HfO}_{(x+y)}$ region, where the latter exhibits a more disordered lattice arrangement, particularly apparent at the interface between the two oxide layers in the HAADF image, suggestive of the emerging monoclinic phase. The simulation results also align with the findings of the FFT analysis in Fig. 3.4, further confirming this transition.

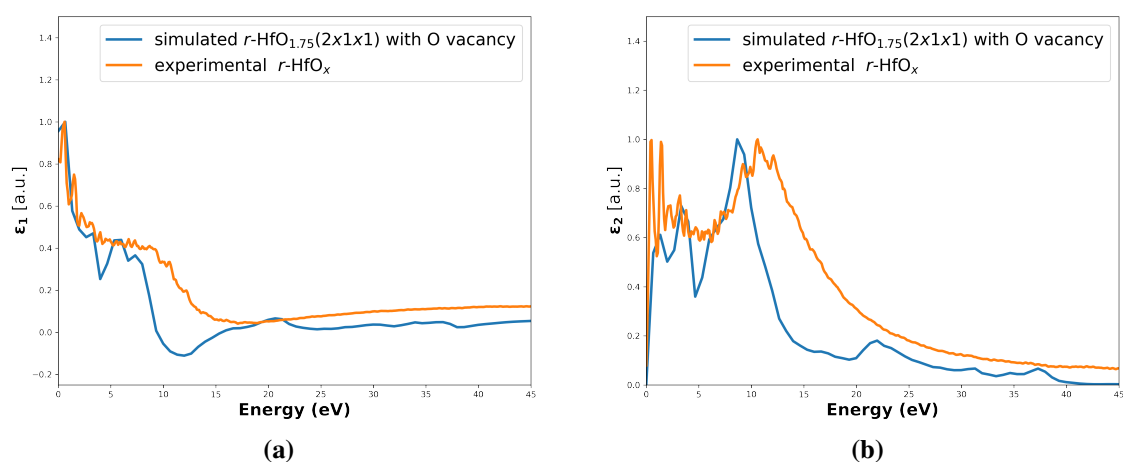


Fig. 3.12 Comparison of experimental and simulated dielectric functions ((a) real, and (b) imaginary) of $r\text{-HfO}_x$ and $r\text{-HfO}_{1.75}$ supercells with oxygen vacancy.

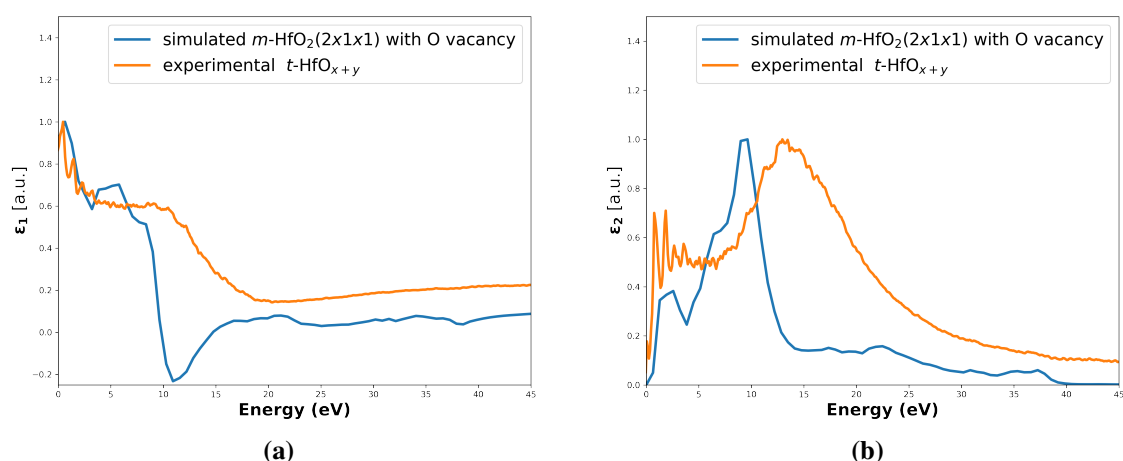


Fig. 3.13 Comparison of experimental and simulated dielectric functions ((a) real, and (b) imaginary) of $t\text{-HfO}_{x+y}$ and $m\text{-HfO}_2$ supercells with oxygen vacancy.

3.7 Discussion

This work in this chapter provides information about structural and electronic properties of hafnia-based RRAM devices and studies the effect of oxygen stoichiometry on the dielectric properties.

The evidence of a dual-layer structure in r-HfO_{1.7} samples, compared to the uniform structure in m-HfO₂, shows how the ambient environment condition affects the RRAM device structure. The rhombohedral-monoclinic phase transition with exposure to air proves that hafnia-based materials are extremely sensitive to the ambient environment.

The FFT analysis of the structural change from R3m to P21/c symmetry gives crystallographic proof that oxidation-induced phase transitions do indeed occur. This is important because it implies that device properties can be tuned locally using controlled oxidation processes.

The correspondence between dielectric response and structural phase depicts that minor variations in oxygen content affect the electronic properties. It is both an opportunity and a challenge: it facilitates fine-tuning of device parameters, yet requires delicate control over fabrication and operating conditions. The correspondence of DFT simulations with experimental EELS data supports our findings as well.

Technologically, these results indicate that oxygen-rich layer formation can be leveraged to develop engineered interfaces with designed dielectric behavior. Control of local stoichiometry of oxygen via ambient exposure or by controlled oxidation processes could be used to develop RRAM devices with enhanced switching performance, endurance, and retention characteristics.

Although this research presents useful information, certain limitations must be noted. The precise quantification of oxygen vacancy concentrations is still challenging, and the effect of other types of defects (e.g., hafnium vacancies or interstitials) on the resulting properties needs to be examined further.

3.8 Conclusions

In this chapter, we analyse the structural and dielectric properties of hafnia-based RRAM devices with varying oxygen content.

- Two types of HfO_x layers, monoclinic (m-HfO_2) and rhombohedral ($\text{r-HfO}_{1.7}$) were fabricated using Molecular Beam Epitaxy under different environmental conditions.
- Structural characterisation using ABF and HAADF-STEM revealed a dual-layer formation in $\text{r-HfO}_{1.7}$, in contrast to the uniform structure in m-HfO_2 .
- EDS analysis confirmed a gradient in the Hf/O ratio in $\text{r-HfO}_{1.7}$, indicating an oxygen-rich top layer due to ambient air exposure, possibly linked to a phase transformation.
- FFT analysis of HRTEM images suggested that oxidation leads to a structural change from rhombohedral to monoclinic phase.
- Dielectric properties of the different layers were studied using EELS and Kramers-Kronig analysis, revealing a significant shift in the dielectric function due to increased oxygen content.
- DFT simulations with oxygen vacancies in m-HfO_2 and $\text{r-HfO}_{1.75}$ structures reproduced the dielectric trends observed experimentally.
- Simulated dielectric functions aligned well with experimental EELS results, supporting the observed phase transition and its influence on dielectric behaviour.
- The formation of an oxygen-rich monoclinic layer upon air exposure opens the potential for engineering dielectric interfaces to enhance RRAM performance.

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Chapter 4

Impact of pressure and charge variations on EEL spectra of embedded xenon gas clusters.

This chapter explores the changes in the EELS features stemmed from the structural modifications of Xenon (Xe) gas clusters encapsulated within graphene. The study examines two specific configurations: clusters composed of five Xe atoms and those containing two Xe atoms. Through DFT-EELS simulations, variations in charge and pressure are systematically introduced to assess their impact on the structural changes within the system and the corresponding EELS spectra.

4.1 Xenon gas clusters: insights and the drive behind this work

Xe is a fascinating noble gas due to its unique properties and diverse applications across critical fields such as research, industry, and medicine [1–3]. In nuclear applications, Xe is both a fission byproduct and a crucial element in nuclear waste management. Innovative approaches, such as trapping xenon in silica nanocages, have been explored for nuclear waste remediation and the nonproliferation of nuclear weapons [4]. Its medical applications include its use as a safe and effective anaesthetic and in medical imaging [5], further demonstrating its inertness and versatility. In dark matter detection, liquid xenon is highly sensitive and has a low energy detection threshold, making it well-suited for detecting weakly interacting massive particles [6]. Xe clusters in helium nanodroplets exhibit unique photoionisation dynamics, where direct inner-shell photoionisation dominates over charge transfer ionisation, primarily forming singly charged Xe ions despite the possibility of higher charge states through Auger decay [7]. Under femtosecond laser excitation, electron emissions increase significantly at low energies due to a two-step ionisation process involving helium ionisation by Xe seed electrons [8]. The ionisation process also shows a steplike intensity threshold for highly charged ions at unexpectedly low laser intensities [9]. Additionally, helium helps xenon clusters reach higher charge levels when hit by strong laser light, without changing their usual electron behaviour. [10].

Xe gas clusters embedded in layers or shells of other materials are achieved using ultralow-energy ion irradiation, where noble gas ions penetrate the first shell but are stopped by the second shell. This confinement creates a "sandwich" structure that stabilises the Xe atoms, preventing their escape and enabling their study at room temperature or higher. Xe gas clusters are gaining significant interest in condensed matter physics and industrial usage. From an industrial perspective, shell-like structures with Xe nano-traps in porous materials exhibit remarkable selectivity and adsorption capabilities, making them highly efficient for separating Xe from other gases like Krypton, a critical process in industries requiring pure gas streams [11]. Furthermore, in plasma discharge technologies, the incorporation of Xe

clusters into flexible polymer matrices has been shown to enhance luminescence, optimise luminance conditions, and reduce operational voltages, paving the way for more efficient and sustainable lighting solutions [12]. These exceptional properties and applications underscore the importance of Xe and make it a gas of significant scientific and practical interest.

In condensed matter physics, embedding Xe clusters in materials like graphene enables detailed structural studies at elevated temperatures, providing opportunities for direct imaging and in-depth analysis of atomic structures and dynamics [13]. In this study, we perform DFT-EELS simulations to investigate two xenon gas clusters embedded within graphene layers, aiming to interpret the effects of charge and pressure observed in experimental EELS data. On the basis of experimental data, we construct the cluster models, incorporate realistic conditions by introducing charge and pressure in the system, and analyse the resulting changes in the simulated spectra. Finally, we compare these results with experimental observations to draw meaningful correlations.

4.2 Experimental observations

The samples were prepared by using ultralow energy ion irradiation technique [13] by the group of Physics of Nanostructured Materials at the University of Vienna. In this process Xe atoms were implanted between graphene sheets. The graphene sheets (exfoliated and chemically vapourised) were irradiated with singly charged ultralow energy (55-65 eV) Xe ions to introduce Xe inside the graphene bilayers. The samples were then observed in a Nion UltraSTEM 100 microscope. The scanning transmission electron microscope - annular dark field (STEM-ADF) images are shown in Fig. 4.1. Xe clusters in multiple groups can be spotted inside a single image. The clusters have no particular order nor a periodicity. For a better view, a collection of multiple Xe clusters collected throughout the sample is provided in Fig. 4.2. Further, EELS measurements were carried out for two clusters (Xe_2 , Xe_5) and are shown in Fig. 4.3. For both the cases, the EELS spectra exhibit distinct features corresponding to the $M_{4,5}$ edges of Xe, thereby confirming its presence as isolated gas clusters.

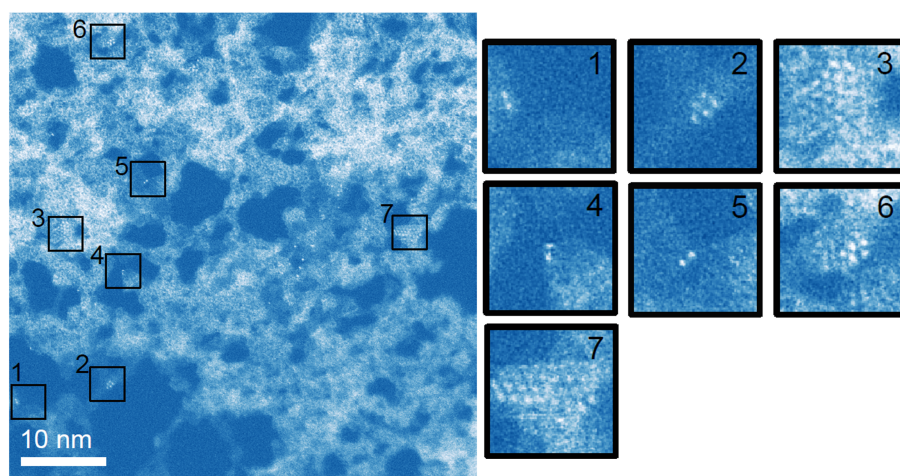


Fig. 4.1 Double Gaussian Fourier filtered STEM-ADF depicting the spread of Xe gas clusters across the sample [13].

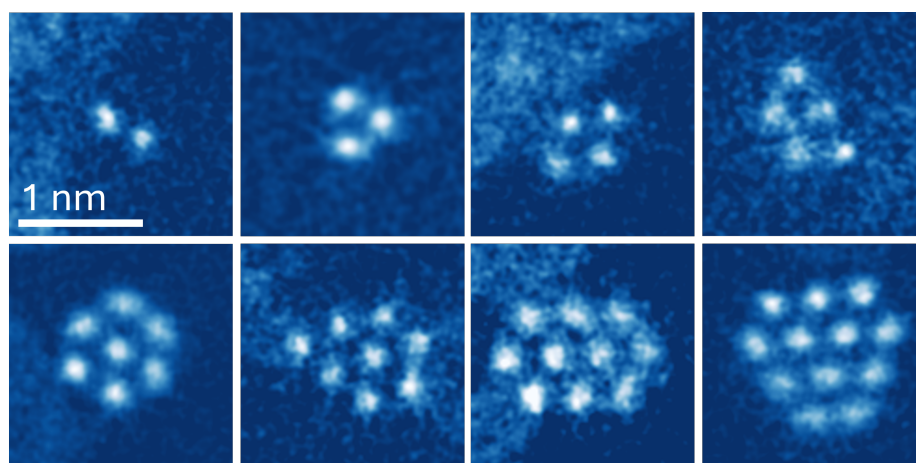


Fig. 4.2 Double Gaussian Fourier filtered STEM-ADF images of Xe gas clusters from 2 to 12 atoms [13].

Due to the presence of graphene around the Xe atoms, the Xe clusters form a 2D shape and are exposed to pressure from the surrounding graphene sheets [13]. Further, the gas clusters, may have charged behaviour as well due to electron beam irradiation during EELS. Both the charge and pressure may have an effect on the EELS of the Xe gas clusters. In order to interpret the effect of these parameters on the experimental EELS results, EELS simulations through DFT were carried out.

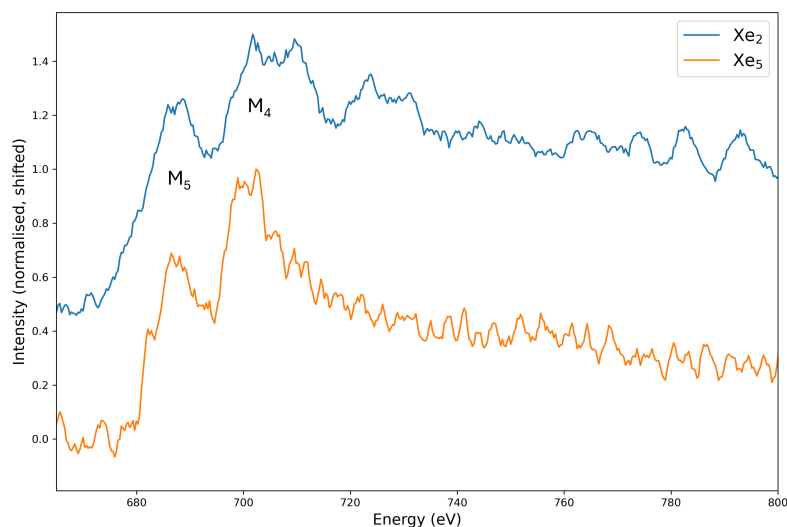


Fig. 4.3 EELS spectra for Xe_5 and Xe_2 gas clusters, depicting the $\text{M}_{4,5}$ edges.

4.3 EELS simulation of Xe gas clusters

Among the various Xe clusters observed in the sample, two clusters containing 2 (Xe_2) and 5 (Xe_5) Xe atoms were selected for EELS simulations. The selection criterion was primarily set by the significant size of Xe atoms, which requires high computational demands. For the simulations, the two-dimensional structures of the clusters were first modelled and structurally relaxed using GPAW [14]. EELS simulations were subsequently performed on the relaxed configurations using WIEN2k [15]. Additionally, further simulations were conducted to investigate the effects of introducing charge and applying pressure to the clusters, providing deeper insights into their EELS signatures.

4.3.1 Simulation structures

For the Xe_2 and Xe_5 , the initial structures were designed based on interatomic distances derived from the experimental images shown in Fig. 4.2. These preliminary structures were then relaxed using the GPAW software [14], employing the Lennard-Jones potential with a cutoff criterion of $0.001 \text{ eV/\AA}$. To simulate the effects of pressure on the system, the

relaxed structures were subjected to external forces of 0.2, 0.4, and 0.8 eV/Å. Following the application of each force, the structures were re-relaxed to account for the influence of pressure. The resulting relaxed configurations, including those under pressure, are presented in Fig. 4.4. The results indicate that increasing pressure causes the Xe atoms to move closer together, leading to a reduction in the interatomic distances.

4.3.2 EELS simulation

EELS simulations were performed on each relaxed structure using WIEN2K [15]. The self-consistent field (SCF) calculations were performed with the energy and charge convergence criteria set to 0.0001 eV and 0.001 e, respectively. Given the non periodic nature of the system, the number of k-points was set at 4, and the RKMax value was set at 6.5. The Perdew–Burke–Ernzerhof (PBE) functional was utilised for the simulations. Further, to study the effect of charge, a charge of +1 and +2 was put into the system by removing one and two electrons from the respective cluster.

4.3.3 EELS simulation results

The EELS simulations were performed individually for each atom in the system, and subsequently, the average spectrum for all Xe atoms was calculated to provide a representative view of the system's electronic structure. The results of these simulations for Xe₂ and Xe₅, accounting for the effects of charge states and applied pressure, are presented in Fig. 4.5 and Fig. 4.6, respectively.

For the study of simulated EELS spectra, changes in the ELNES of the M_{4,5} edges have been selected for observation. In the simulated spectra, it exhibits distinct spectral modifications that correlate with variations in pressure and charge state. For all the charge states, as the pressure increases, the M_{4,5} edges become sharper with further fine structures being visible as well. This indicates that the application of pressure significantly influences the local electronic environment of Xe atoms, possibly through changes in bond lengths, coordination, or local field effects.

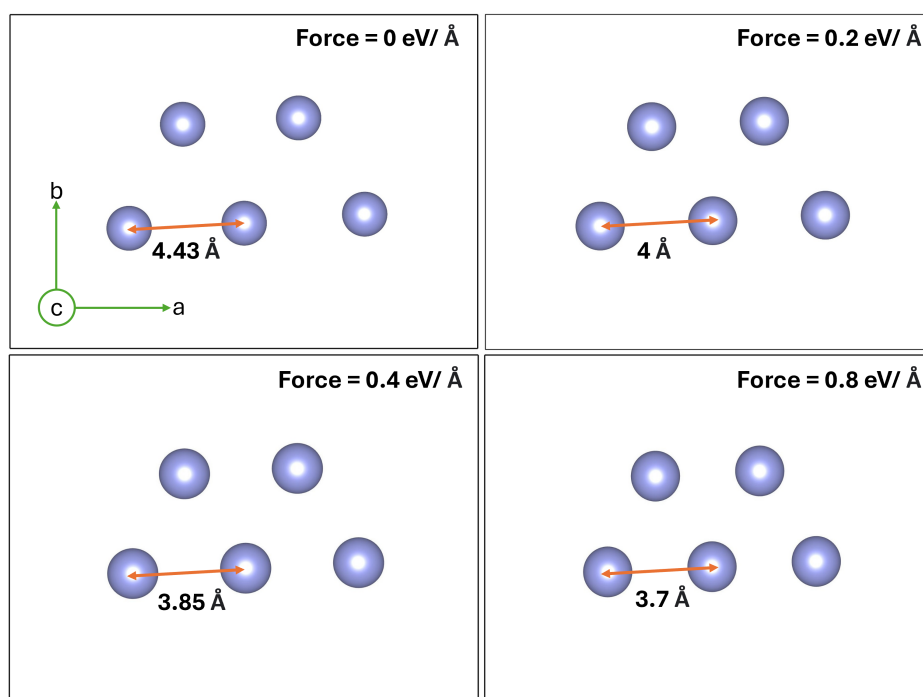
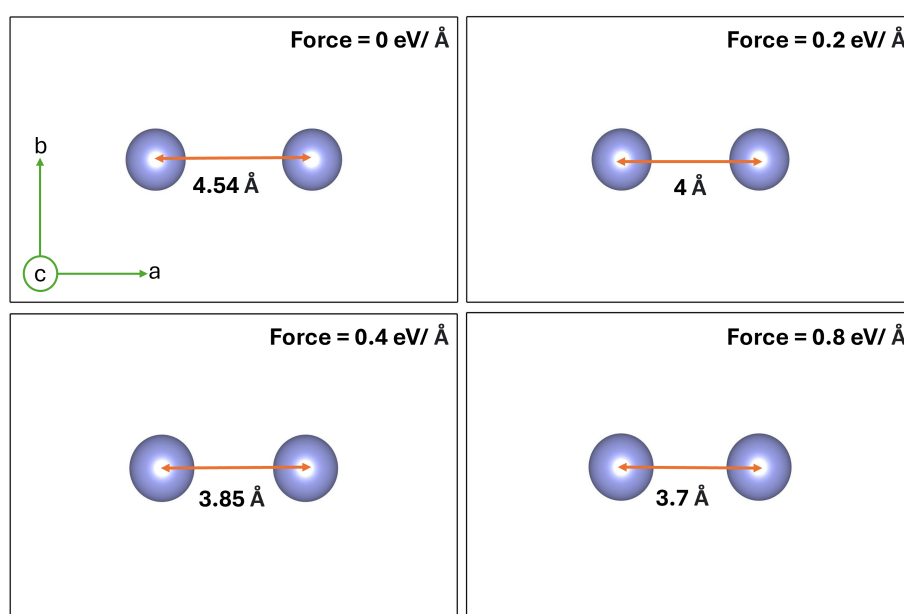
(a) Xe₅ cluster.(b) Xe₂ cluster.

Fig. 4.4 Xe cluster structures with force variations and the corresponding interatomic distance after relaxation of the structure.

A similar yet more prominent effect can be observed when higher charge states are introduced to the system. The $M_{4,5}$ edges along with their fine structures, can be seen evolving as the charges increase. This suggests that the electronic perturbations introduced by charging further enhance the sensitivity of the system to applied pressure. The pronounced splitting in higher charge states could be attributed to increased electronic repulsion or redistribution of the electron density within the system, which modifies the excitation probabilities in the EELS process.

The interplay between charge and pressure introduces a complex dependency, where higher charge states and increased pressure introduces spectral changes. These observations highlight the sensitivity of EELS to subtle changes in the local environment and opens the door to valuable insights into the electronic and structural characteristics of Xe clusters under varying external conditions.

4.4 Comparison of EELS simulation with experimental data

The comparison of experimental and the simulated EELS data are presented in Fig. 4.7 and Fig. 4.8 for Xe_2 and Xe_5 , respectively. Only the pressure states of 0.4 and 0.8 eV/Å have been considered for the comparison, as the states of 0 and 0.2 eV/Å clearly show relatively less features, as observed in Fig. 4.5 and 4.6. EELS simulations performed using WIEN2K often need a recalibration of the energy axis due to various factors, including relativistic calculations, broadening effects, and initial parameters [16–19]. Consequently, to improve the fit, the simulated spectra have been slightly shifted by about 2 and 6 eV towards lower energy for Xe_2 and Xe_5 respectively.

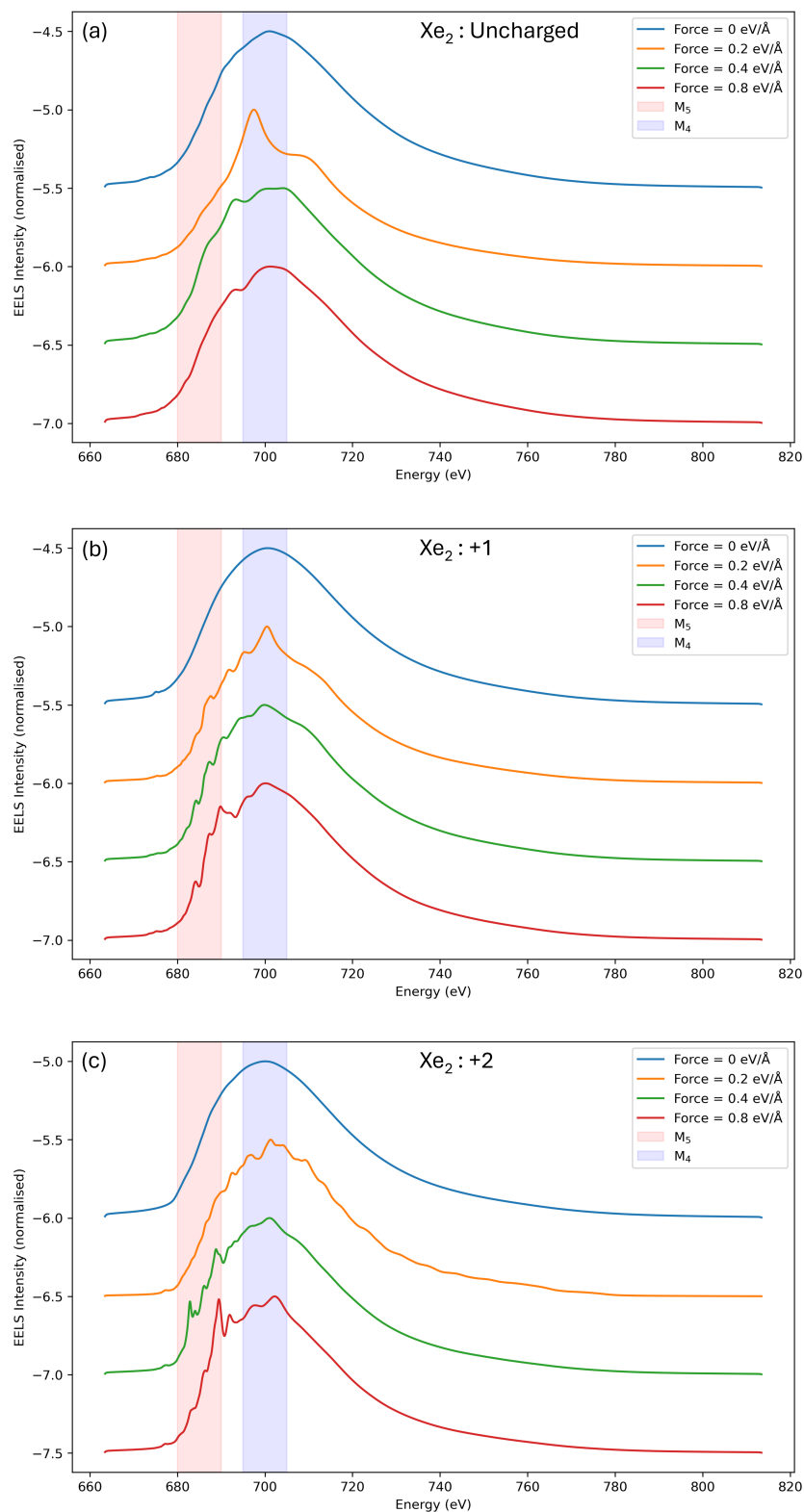


Fig. 4.5 Xe_2 EELS simulation with charge (a) 0 (b) +1 (c) +2 and four pressure (force) variations. The introduction of charge and pressure introduce changes in the $M_{4,5}$ region.

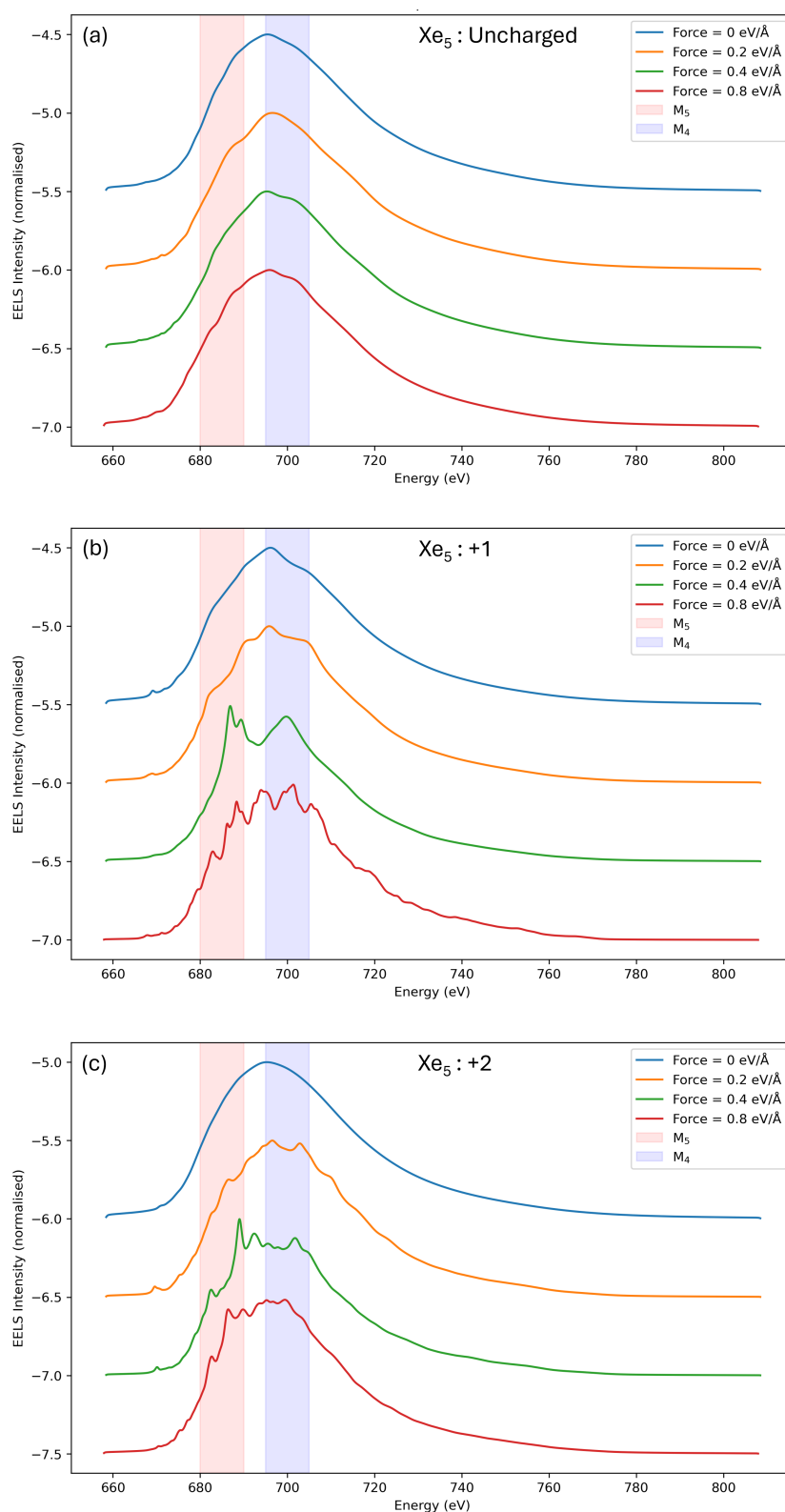


Fig. 4.6 Xe_5 EELS simulation with charge (a) 0 (b) +1 (c) +2 and four pressure (force) variations. The introduction of charge and pressure introduces changes in the $M_{4,5}$ region.

For a better comparison, the relevant features (named as A, B, C, D, and E on the plots), along with the relative peak heights in the M_5 and M_4 energy regions have been considered. For both the cases of Xe_2 and Xe_5 , besides the main edges, more features can be seen in the +2 charge state than in the +1 charge state.

For Xe_2 , the comparison between the experimental and simulated EELS data for both force values of 0.4 and 0.8 $\text{eV/\AA}$ in the +1 & +2 is in relative good agreement with the experimental EELS data. It can be observed that for both the pressures, in the +1 and +2 state, features A, B, and C show a good match. However, features D and E align more closely with the 0.8 $\text{eV/\AA}$ with +2 charge than the 0.4 $\text{eV/\AA}$ with +2 charge.

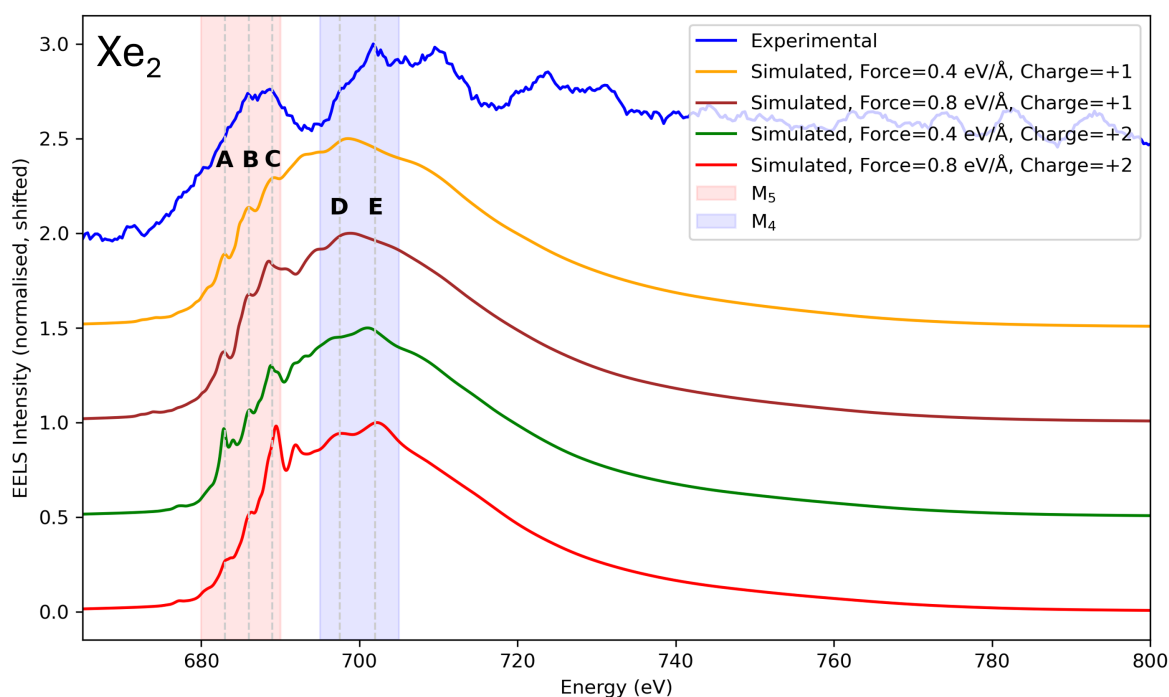


Fig. 4.7 Xe_2 comparison of experimental and simulated EELS data. Spectral features (A, B, C, D, and E) have been marked for an easier comparison between the plots.

Similarly, for Xe_5 , in the M_5 region, the simulated EELS spectra for both force values of 0.4 and 0.8 $\text{eV/\AA}$ in the +1 and +2 charge states tend to fit the experimental data. For the 0.4 $\text{eV/\AA}$ case, only two features (B, C) for +1 charge and (A, C) for +2 charge match the experimental data, whereas for 0.8 $\text{eV/\AA}$, all three features (A, B, and C) for the +2 charge

match the experimental data. Furthermore, the relative heights between the M_4 and M_5 edges correspond more closely with the $0.8 \text{ eV/\AA}$, $+2$ case. All these observations suggest that the simulated data for $0.8 \text{ eV/\AA}$ with a $+2$ charge state provide closer agreement with the experimental data than the others. In the M_4 region, both experimental and simulated data exhibit fine structures (D, E). However, a direct and precise correspondence between them is difficult to establish due to subtle variations. For example, feature D in the experimental data is a good match for the $0.8 \text{ eV/\AA}$ with $+1$ and $+2$ charge states as well as the $0.4 \text{ eV/\AA}$ with $+1$ charge but none of them is a good fit for the feature E. Similarly, feature E in the experimental data aligns well with the $0.4 \text{ eV/\AA}$ with $+2$ charge but the feature D in the same case does not.

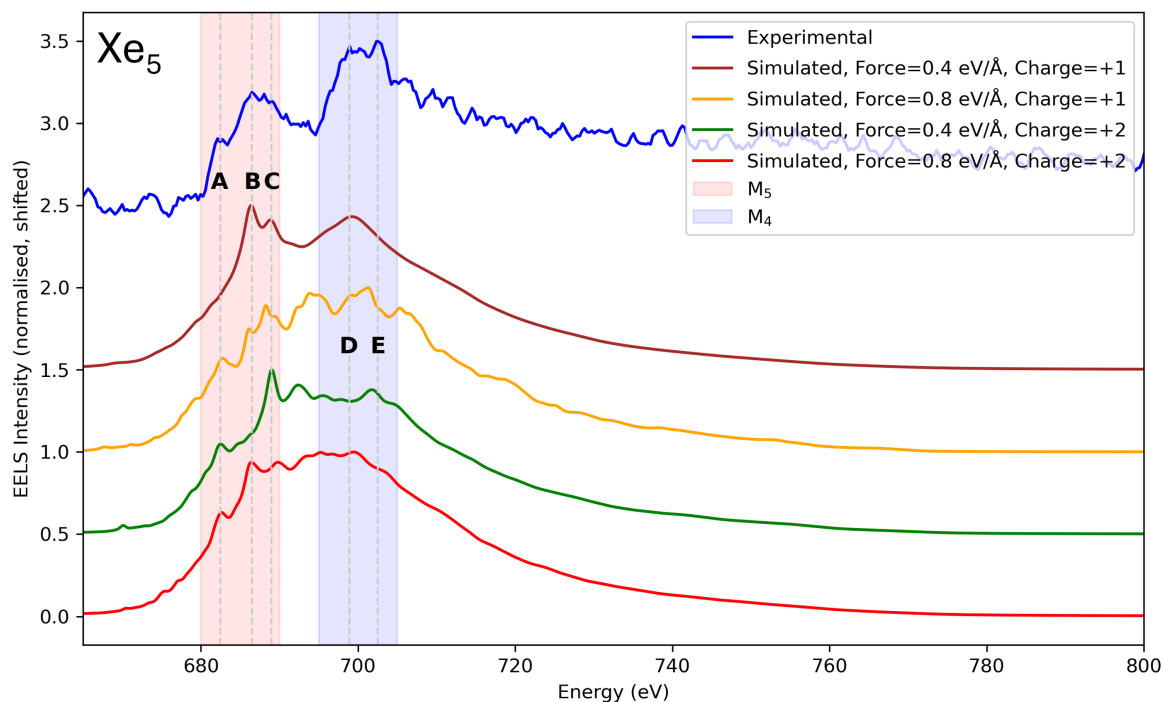


Fig. 4.8 Xe_5 comparison of experimental and simulated EELS data. Spectral features (A, B, C, D, and E) have been marked for an easier comparison between the plots.

It is worth noting that the minor discrepancies observed in the simulations highlight the intricate nature of the system and suggest that, while the simulations give us an idea about the effect of pressure and charge on the EELS, further refinements could enhance the accuracy

of relative peak intensities and ELNES. In particular, incorporating the effects of graphene, though computationally demanding, presents an exciting avenue for future improvements. Additionally, the $M_{4,5}$ edge fine structure is less striking in the simulations, which can be attributed to the inherent design of WIEN2K, as it is primarily optimised for solids [15]. In bulk materials, the presence of a larger number of atoms leads to stronger electronic interactions, naturally enhancing spectral features such as peak splitting. However, in our case, the relatively small number of atoms in the confined Xe clusters results in weaker interactions, making the splitting less prominent. Despite this, the overall trends remain consistent, and further refinements in computational methods could provide even greater accuracy in modelling such clusters.

Overall, by combining DFT-EELS simulations with experimental data, we have explored how external influences, such as confinement effects (pressure, charge) modulate the spectral features of Xe clusters.

4.5 Discussion

This chapter illustrates the fruitful use of DFT-EELS simulations to investigate electronic structure changes of confined noble gas clusters. Systematic investigation of pressure-induced effects in Xe clusters indicates that confinement distinctly alters the local electronic surroundings, as shown by the development of $M_{4,5}$ edge fine structure with the increased applied pressure. The fact that spectral properties become more defined and sharp at higher pressure implies that atomic compression alters the density of states at the Fermi level.

These observations are important for explaining how two-dimensional confinement between graphene sheets influences the intrinsic properties of noble gas atoms, which are otherwise considered chemically inert. The fact that the charge states provide the best match with experiment indicates that the electron beam irradiation carried out during EELS measurements largely influences the charge configuration in these small clusters.

The good correlation of DFT-EELS simulations and experimental findings justifies the computational method in the investigation of such trapped atomic arrangements. The

consistency of simulated and experimental spectral characteristics proves that first-principles calculations can be used to help predict the electronic response of matter in non-standard conditions.

These findings add to the general understanding of how confinement in dimensions impacts atomic properties. The capacity to alter the electronic structure in noble gases using geometric restriction provides prospects for creating new functional materials in which inert elements may have vital functions.

4.6 Conclusions

Overall, the findings of the study can be summarised as the following.

- This study investigated the impact of pressure (0.2, 0.4, and 0.8 eV/Å) and charge (0, +1, and +2) on the EELS spectra of embedded Xe₂ and Xe₅ gas clusters using DFT-EELS simulations and experimental comparisons.
- STEM-ADF imaging and EELS measurements confirmed the presence of Xe clusters inside graphene layers, providing a reference for theoretical simulations.
- Structural relaxation of the clusters was performed using GPAW, and EELS spectra were simulated using WIEN2K, incorporating charge and pressure variations to replicate experimental conditions.
- Increasing pressure (0.4 and 0.8 eV/Å) led to a splitting of the M_{4,5} edges, demonstrating a significant impact on the local electronic structure of Xe atoms.
- Higher charge states (+1 and +2) modified the spectral features further, with +2 charge at 0.4 – 0.8 eV/Å showing the best agreement with experimental data for both Xe₂ and Xe₅ clusters.
- With the increase in computational facilities, further refinements in the simulations can increase the accuracy, thereby enabling a deeper understanding of the physics of noble gas clusters.

4.7 References

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Chapter 5

Quantification of antisite defects in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) thin films using high angle annular dark field (HAADF) simulations

This chapter presents a framework for quantifying antisite defects in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin films through HAADF-STEM imaging and simulations. It starts by modelling the defects and conducting image simulations, followed by a comparison of experimental images with simulation results to determine the defect density. The study emphasizes the impact of growth conditions on defect density and offers a practical method for defect quantification.

5.1 Introduction and motivation for the study

Complex oxide thin films are attracting significant interest due to their wide-ranging applications in energy and information technologies. These materials are essential in devices like electron and ion conductors [1], photovoltaics [2], thermoelectrics [3], dielectrics [4], and resistive switching systems [5]. They are strongly influenced by grain boundaries, cationic composition, and defect chemistry. Grain boundaries alter electronic and oxygen transport by modifying cation concentrations at interfaces while the local non-stoichiometry in defect chemistry affects electrical resistance, particularly under varying oxygen partial pressures. [6]. Transition metal oxides with ABX_3 perovskite structure can exhibit exceptional properties like superconductivity, magnetoresistance, ionic conductivity, multiferrocity, and piezoelectricity [7–17].

Amongst the perovskite structures, $La_{1-x}Sr_xMnO_3$ (LSMO) has gained significant attention in many research fields due to its unique combination of properties that make it particularly advantageous for various applications. One of the key factors is its low carrier density coupled with a high Curie temperature, which, together with its strong spin polarisation and intrinsic ferromagnetic properties, positions LSMO as an ideal material for spintronic devices [18–24]. The material exhibits a decrease in resistivity upon cooling, linked to a transition from a paramagnetic to a ferromagnetic state [25, 26]. This transition is of particular interest because it leads to a phenomenon known as colossal magnetoresistance, characterised by a substantial negative magnetoresistance at the Curie temperature [27, 19]. Furthermore, the ability to tailor LSMO resistance with low bias makes it highly suitable for applications in tunable radio frequency technologies [28]. It also finds its applications in solid oxide fuel cells [29, 30], upcoming data storage technology, and advanced logic devices [12, 31–36]. Beyond its electronic applications, LSMO nanoparticles have also shown significant potential in the biomedical field such as hyperthermia for cancer treatment [37, 38] and drug delivery systems [39], further establishing its versatility and promise for advancing research across multiple scientific disciplines.

A typical perovskite structure has the formula of ABX_3 where A is usually a large cation, B is a small cation and X is an anion. A sample of $SrTiO_3$ structure is shown in

Fig. 5.1. In the case of LSMO, La and Sr occupy the A site, Mn and O occupy the B and X sites, respectively, as shown in Fig. 5.2. Defects in LSMO are very prominent and are known to have a significant impact on their functionality [40], such as defect-induced spin deterioration [41], and magnetic bi-states phenomena [42]. Amongst the possible defects, antisite defects are a particular type of crystal defect where atoms occupy incorrect lattice positions [7]. In the context of LSMO, antisite defects effectively mitigate the impact of cationic nonstoichiometry on oxygen mass transport properties [43]. Antisite defects affect both, the oxygen diffusivity as well as the concentration of oxygen vacancies [43], making it an important criterion to be studied further. In LSMO, La (A site) occupies a few positions of Mn (B site) as shown in Fig. 5.2. This is because Mn can present multiple valencies (Mn^{3+} , Mn^{4+}), whereas La exhibits only one valence state (La^{3+}) [24]. This allows La to occupy the position of Mn, but not the other way round. Additionally, the high structural stability of Mn facilitates large-scale doping. Owing to this defect, the transport and magnetic properties are highly affected. The defect density can be adjusted to meet specific electrochemical property requirements by tailoring growth conditions, including external pressure, oxygen stoichiometry, and Sr doping [44]. These defects can have low formation energies and are often magnetised, potentially affecting spintronic applications and redox catalysis [7, 45]. Such studies emphasise the crucial role of antisite defects and the need for quantification methods.

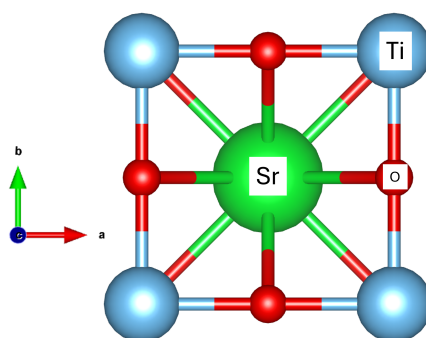


Fig. 5.1 SrTiO_3 structure. Sr, Ti, and O are located in the A, B, and X sites of an ABX_3 perovskite respectively.

Antisite defect quantification has been performed for various compounds using a range of methods. For Zr_2Cu , in situ X-ray diffraction coupled with molecular dynamics simulation has been employed to quantify antisite defects during crystallisation [46]. Techniques such as electron spin resonance, infrared absorption, and magnetic circular dichroism have been applied to investigate antisite defects in GaAs [47]. In LaAlO_3 , temperature-dependent Raman and optical absorption spectroscopies have been utilised for studying these defects [48], while time-resolved synchrotron X-ray diffraction has been used for similar investigations in LiFePO_4 [49]. Additionally, Rietveld refinement analysis has proven effective in examining antisite defects in LiNiPO_4 [50]. High-angle annular dark-field (HAADF) and annular bright-field (ABF) in scanning transmission electron microscopy (STEM) have enabled the direct visualisation of antisite defects in LiCoPO_4 nanocrystals [51]. Furthermore, efforts have been made to observe, control, and quantify antisite defects in several oxides, including $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ [52], $\text{Sr}_2\text{FeMoO}_6$ [53] and $\text{Y}_3\text{Al}_5\text{O}_{12}$ [54] [55]. However, there have been limited attempts to quantify antisite defects in LSMO.

HAADF-STEM in aberration-corrected microscopes enables atomic-resolution Z-contrast imaging, where the image intensity scales with the atomic number (Z) raised to an exponent α , typically ranging from 1.4 to 2 [56, 57]. Heavy elements appear noticeably brighter than lighter ones due to incoherent electron scattering at high angles, which is the primary cause of contrast in HAADF images. This makes it easier to distinguish and identify atomic columns in complex materials [58]. Atomic number, specimen thickness, and microscope parameters like detector angles are some of the variables that affect HAADF contrast [59, 60]. When detector angles (and other parameters) are fixed, increasing the sample thickness leads to higher background intensity, which needs to be subtracted for better accuracy in quantitative analysis [59]. In the case of LSMO, the differences in atomic number between La ($Z=57$), Sr ($Z=38$), and Mn ($Z=25$) make HAADF-STEM an ideal tool for detecting these defects in LSMO. Changes in the composition should affect the intensity of the atomic columns in the HAADF images. Using this principle, site occupancies and defect concentrations have been studied, particularly in systems where the local intensity is modulated by antisite substitutions or mixed occupancies. For instance, Chung et al. [61] directly visualised antisite

defects in LiFePO_4 using atomic-resolution HAADF imaging and multislice simulations, comparing measured intensity variations with modelled occupancy levels. Similarly, in order to measure cation column occupancy and identify light-element vacancies, Findlay et al. [62] quantified the HAADF intensity in SrTiO_3 and BaTiO_3 . They were able to determine occupancy factors with a few percent accuracy by comparing experimental profiles with frozen phonon simulations. Further, Van Aert et al. [63] used HAADF contrast imaging combined with statistical parameter estimation to quantify atom counts in GaN and AlN columns by mapping calibrated atomic column intensities. While HAADF-STEM has been successfully applied to study antisite defects in other materials [7, 61, 64], its application to LSMO, particularly with respect to the quantification of the antisite defect, has been unexplored.

Here we propose a method for the quantification of antisite defects in experimental HAADF images through image simulation. Further, we use the methodology to quantify the defects in the experimental LSMO samples fabricated under different preparation conditions, leading to variable amounts of antisite defects. Our study aims to establish a method for correlating experimental observations with defect quantities, thereby facilitating more accurate and comprehensive analysis of antisite defects in large regions of a given specimen.

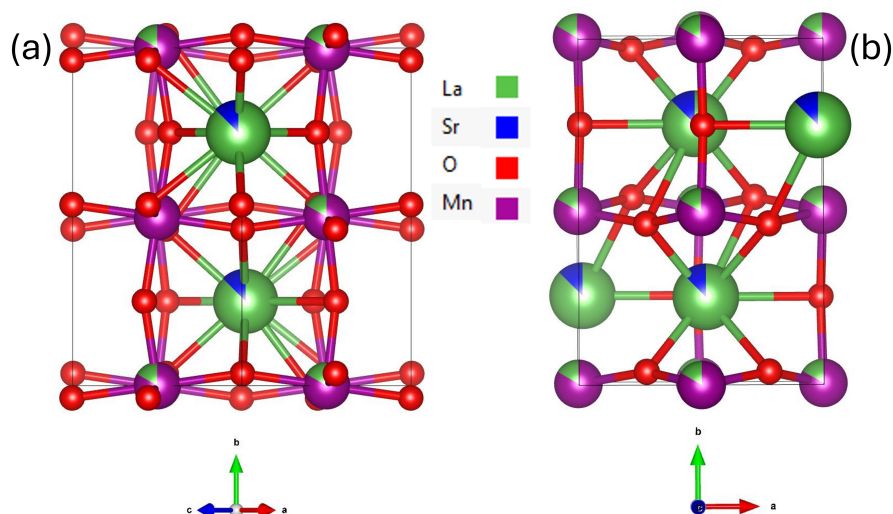


Fig. 5.2 Orthorhombic unit cell of LSMO in two orientations (a) [101] & (b) [001].

5.2 Methodology

5.2.1 Experimental sample preparation

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_y\text{O}_{3\pm\delta}$ samples were grown at the Catalonia Institute for Energy Research (IREC), by the group of Albert Tarancon and co workers. The films were grown on SrTiO_3 (001) single crystal substrates (Crystec GmbH) by Pulsed laser Deposition (PLD) using a large area PLD system (PVD Systems-PLD 5000) equipped with a 248 nm KrF excimer laser (Lambda Physics-COMPex PRO 205). LSM_y thin films were grown at 700 °C with an energy fluence of 1 J cm^{-2} per pulse, a frequency of 10 Hz, and a substrate-target distance of 95 mm. The Mn/(La + Sr) ratio was varied by controlling the background pressure during deposition. Indeed, as demonstrated in our previous work [43], an oxygen background pressure of $p\text{O}_2 = 2.6 \times 10^{-2}$ mbar can be used to grow nearly stoichiometric LSM layers ($y \sim 1.00$), while highly Mn-deficient thin films ($y \sim 0.85$) are obtained for $p\text{O}_2 = 6.6 \times 10^{-3}$ mbar. The samples were in-situ annealed in 0.3 mbar of oxygen at 700 °C after deposition to compensate for oxygen deficiency in the layers.

5.2.2 Image simulation

Apart from the antisite defects ($\text{La}_{\text{Mn}}^\times$), LSMO also contains various types of vacancies and defects, they include B-site vacancies (V_{Mn}'''), A-site vacancies (V_{La}'''), oxygen vacancies ($\text{V}_{\text{O}}^{\bullet\bullet}$), and positively charged defects ($\text{Mn}_{\text{Mn}}^\bullet$), as reported in [43]. The concentration of these defects and vacancies is illustrated in the Brouwer diagram shown in Fig. 5.3. At a working pressure of 0.3 mbar, the concentration of $\text{La}_{\text{Mn}}^\times$ is approximately three orders of magnitude higher than that of V_{Mn}''' and V_{La}''' , and about seven orders of magnitude higher than that of $\text{V}_{\text{O}}^{\bullet\bullet}$. Since the focus of this study is on analysing the intensity of atomic columns in HAADF images, only the $\text{La}_{\text{Mn}}^\times$ defect has been considered, as the contribution of the other defects is expected to be minimal in the imaging results.

To simulate the antisite defects, LSMO crystallographic structures were atomically modelled for HAADF image simulation with varying amounts of antisite defects only, (as shown in Table 5.1). The value of y is a measure of the ratio of the total amount of Mn in

the sample to the sum of the total amount of (La and Sr) in the A site and the amount of La in the B site of the sample, as shown in equation 5.1. The crystallographic modelled structures for two different zone axes, [101] and [001] are shown in Fig. 5.2. The fractional occupancy of the La atom in Mn atomic columns (i.e. A site atoms in B columns) depicts the antisite defects and represents the average composition along the atomic columns in the case of image simulation. Similar models were designed for each value of y .

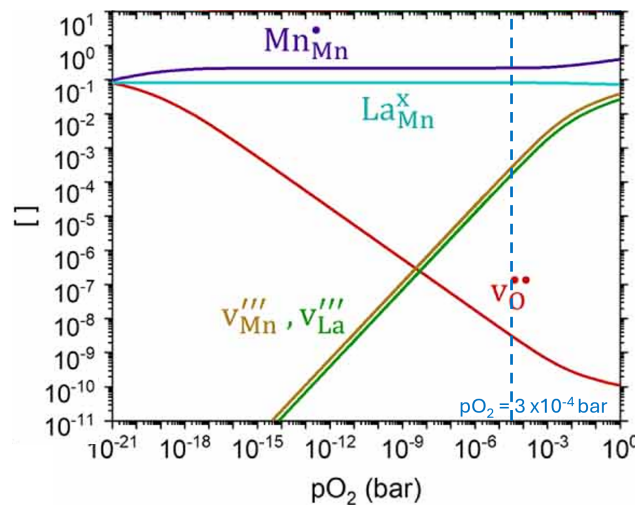


Fig. 5.3 Brouwer diagram representing the concentration of various defects and vacancies in LSMO with $y = 0.85$, adapted from [43].

The STEM HAADF image simulations were conducted using the multislice algorithm of Dr. Probe [65] for the zone axes of [101] & [001]. The thickness of the sample was set in the range of 50-100 nm with an increment of 10 nm in each simulation. The acceleration voltage was set at 200 kV and the convergence semiangle at 24.1 mrad. The HAADF detector was setup with an outer angle of 250 mrad and an inner angle of 80 mrad. Along the z direction, the number of slices and variants per slice per unit cell was set at 4 and 100 respectively. An example of HAADF image simulation with $y = 0.88$ is shown in Fig. 5.4.

$$y = \frac{\text{Total amount of Mn in the sample}}{\text{Total amount of [(La + Sr) in A site + La in B site]}} \quad (5.1)$$

y	La (%)	Mn (%)
0.78	12.4	87.6
0.80	11.1	88.9
0.85	8.1	91.9
0.88	6.4	93.6
0.92	4.2	95.8
0.94	3.1	96.9
0.99	0.5	99.5

Table 5.1 Composition of B site in LSMO with varying y .

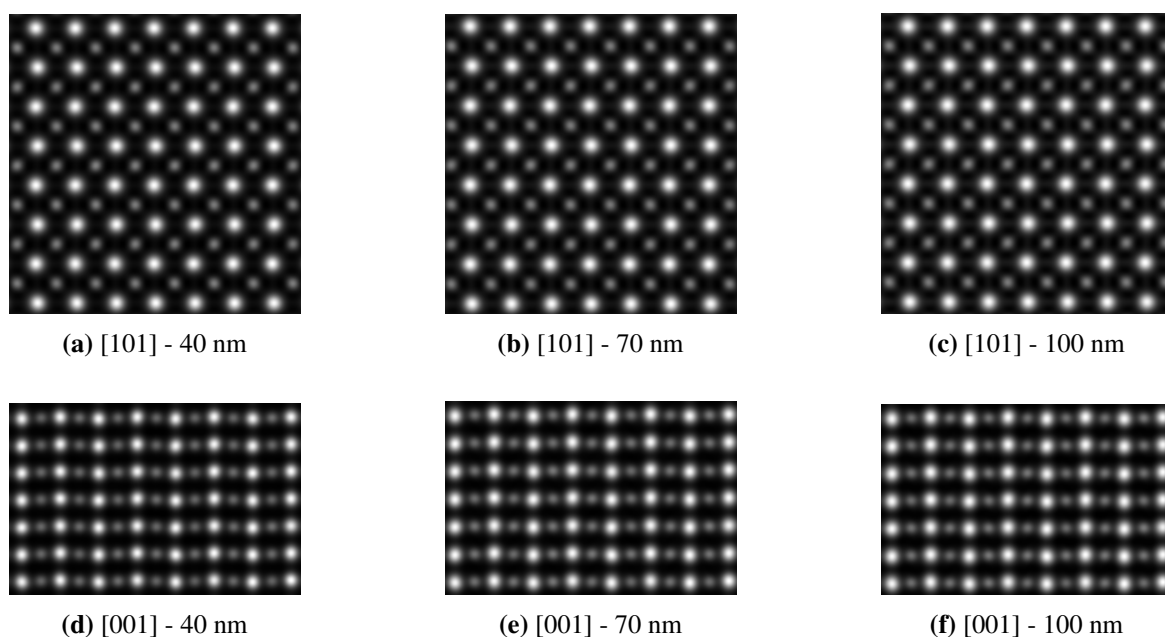


Fig. 5.4 HAADF image simulation of LSMO with $y = 0.88$ for two zone axes and different sample thickness. The brighter white columns correspond to A site and the less bright to B (defective column) site.

Once the HAADF images were simulated, the column intensities of A and B site were integrated using the ATOMAP [66] software, by using the Voronoi method [67] to integrate signal around the atomic columns in the lattice. The radius of each column was measured to account for the intensity from the corresponding atomic column while avoiding contributions

from neighboring columns. In order to account for the background signal, a background intensity was also calculated in between two A sites as shown in Fig. 5.5. The radius of this was chosen as half of that of the A and B sites, while the radius of A and B were kept identical.

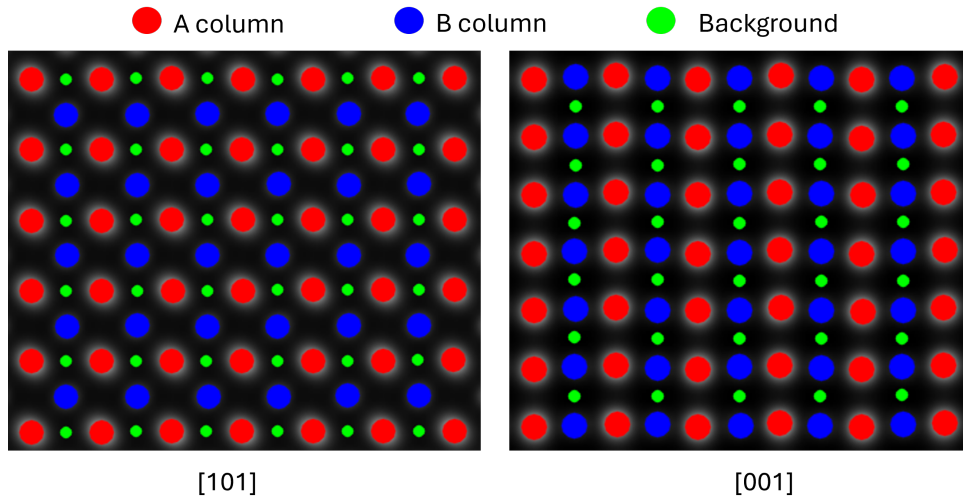


Fig. 5.5 Schematic representation of A, B, and background sites used for HAADF image analysis. The site intensities were integrated using the Voronoi method in ATOMAP.

For each simulation, these intensities of columns A, B and the background were measured and a relative intensity ratio (RIR) parameter was calculated as follows.

$$\text{RIR (Relative Intensity Ratio)} = \frac{(\text{Avg. A site intensity} - \text{Avg. B site intensity}) \times 100}{\text{Avg. A site intensity} - \text{Background intensity} \times 4}$$

Background signal is multiplied by the square of the integration radius ratio (here 2^2) in order to have the same area as the integrated A and B positions. This ratio takes into account the change in intensity of B site due to the presence of the antisite defects by taking the A site intensity as a reference.

Following which, we implemented the ATOMAP A, B and background intensity integration on the experimental images, calculated their RIR and compared that with our simulation to evaluate the density of antisite defect in our experimental sample.

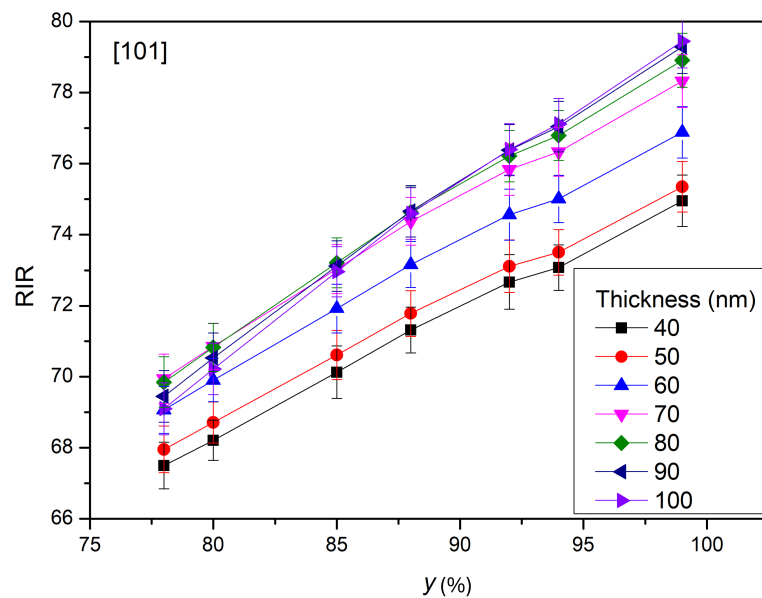
5.3 Simulation results

The intensity of the columns in a HAADF image depends on the thickness, atomic number and the density of the atoms in that particular column. The dependency of RIR on thickness was evaluated by doing the HAADF simulations from 40 nm to 100 nm in steps of 10 nm for two zone axes [101] and [001]. The results are shown in Fig. 5.6. This plot reveals that the RIR is dependent on the thickness of the material. The change in the differences in the RIR of the two zone axes for the same thickness can be attributed to the fact that in the zone axis [001] the effective number of La and Mn atoms are lower than that of [101] and with higher thickness, the difference in the number of atoms increases as well, affecting the RIR. However, in general, it can be concluded that as the value of y increases, the RIR also increases. This chart serves as the basis for the quantification of antisite defects from the experimental images.

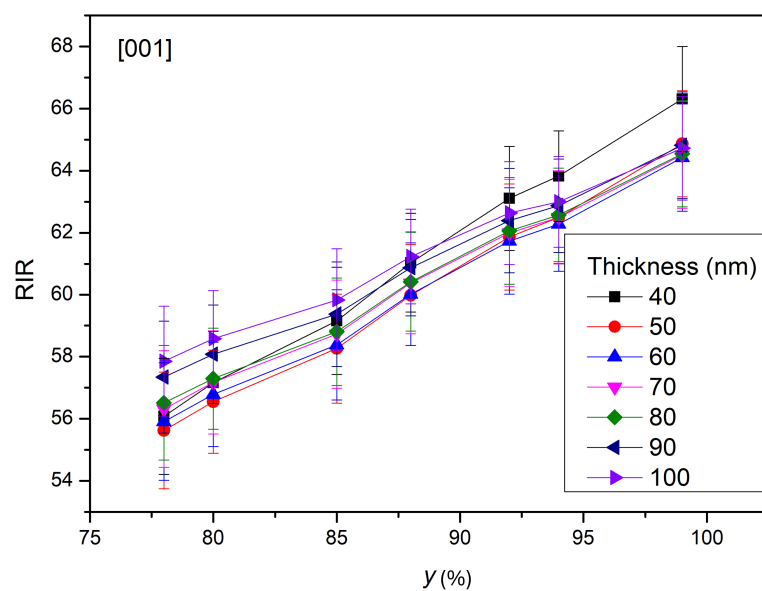
5.4 Experimental results

Two samples were studied, one fabricated with an oxygen partial pressure of 2 mTorr and another with 5 mTorr. These will hereafter be referred to as the 2 mT and 5 mT samples, respectively. The cross sections of the two samples were prepared in the standard FIB procedure and along the [101] zone axis. The lamellae were then observed in a FEI Titan 3 Themis 60-300 microscope operated at 200 kV. The HAADF images, along with its corresponding experimental FFT and the theoretical diffraction pattern are shown in Fig. 5.7. In both cases, the A and B sites are well resolved. EELS log-ratio relative thickness determination was also carried out on low-loss spectra to calculate the thickness of the samples. The t/λ ratio spread across the sample is shown in Fig. 5.8. It can be observed that the t/λ is quite uniformly spread throughout the sample with an average value of 0.57 for 2 mT and 0.70 for 5 mT with a standard deviation of 0.01 and 0.03 respectively. It also reveals the fact that our samples have uniform thicknesses. The mean free path was calculated by following the methodology proposed by Lakoubovskii et al. [68] and Egerton [69] and was found to be 109.142 nm. Using the t/λ ratio and the mean free path, the thickness of the

sample was calculated. The thickness of the 2mT and 5mT samples was calculated to be 62 nm and 76 nm respectively, with standard deviations of 1 nm and 3 nm.



(a)



(b)

Fig. 5.6 Variation of RIR as a function of thickness of the sample and y , for two zone axes (a) 101 and (b) 001.

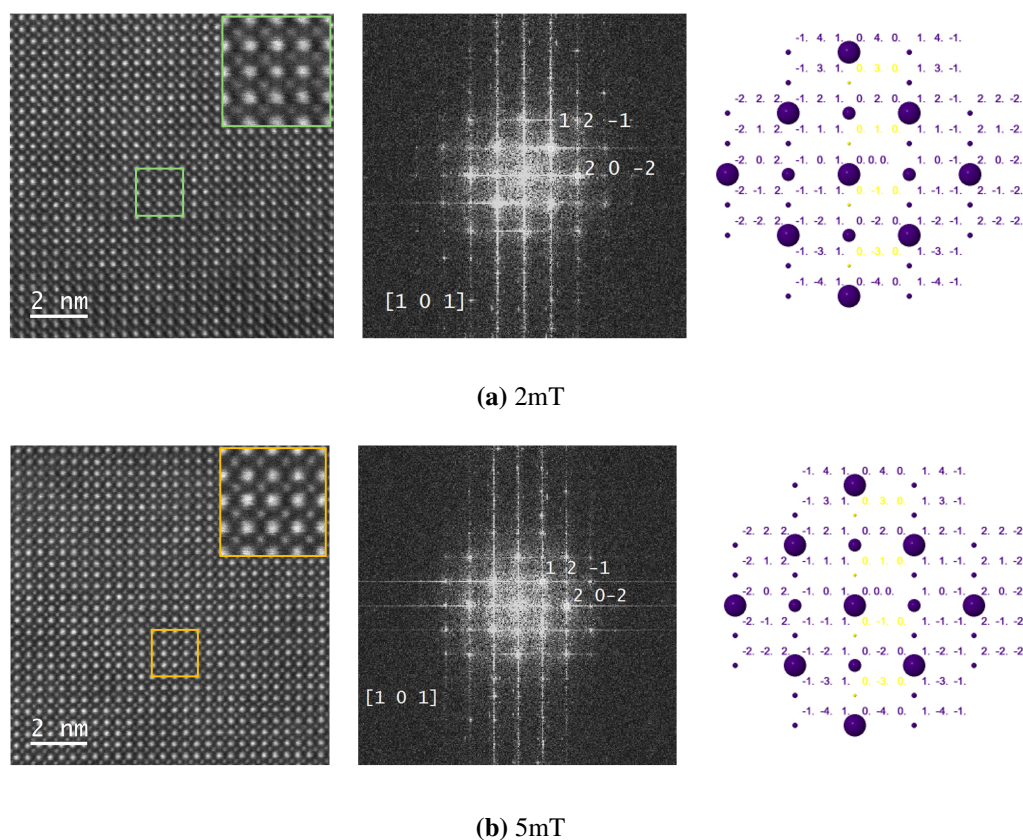


Fig. 5.7 HAADF experimental image (left) with its corresponding FFT (centre) and the theoretical diffraction pattern (right) of (a) 2mT and (b) 5mT. The analysis reveals that the experimental samples have been observed along [101] zone axis.

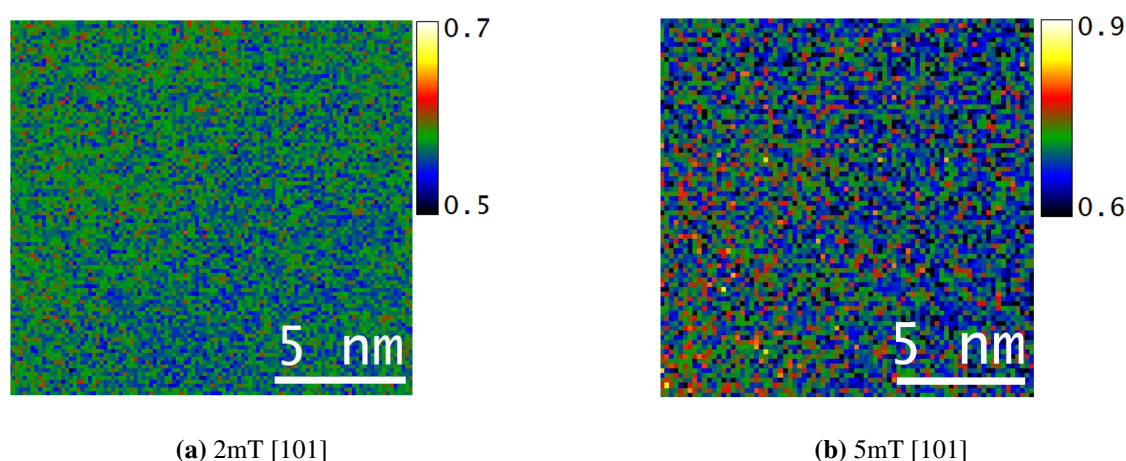


Fig. 5.8 t/λ distribution across the sample for (a) 2mT [101] and (b) 5mT [101]. The distribution is well spread, confirming the uniform thickness of the samples.

5.5 Antisite quantification on experimental results

ATOMAP analysis was performed on all the HAADF experimental images for each sample. The A and B columns were identified as well as the background intensity site, as shown in Fig. 5.9 for the sample of 2mT, and their integrated intensities were evaluated. Subsequently, the RIR was calculated for each HAADF image of a particular sample, and the average RIR was determined. The average RIR value of 2mT and 5mT was evaluated to be 73.7 ± 1.4 and 75.9 ± 0.8 respectively.

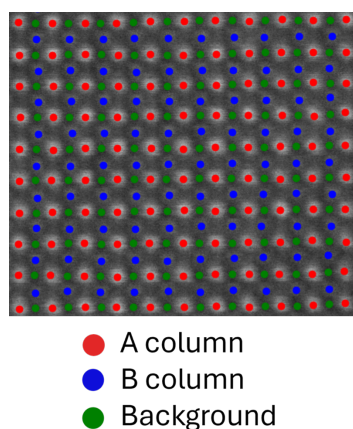


Fig. 5.9 Representation of A, B and Background intensity sites on the experimental HAADF image of 2mT in [101] direction.

Once the thicknesses of the experimental samples were determined, the relationship between RIR and y for each specific thickness needed to be established for defect quantification. To achieve this, the simulated data presented in Fig. 5.6(a) was used to interpolate the corresponding plots for 62 nm and 76 nm thicknesses. Linear interpolation was performed using the data for 50-60-70 nm thicknesses to obtain the 62 nm profile, and the 70-80-90 nm thicknesses to derive the 76 nm profile. The resulting RIR vs. y profiles are shown in Fig. 5.10. It can be observed that the plots in this graph can be fit well with a linear equation.

To evaluate the antisite defect quantification in the samples, the previously obtained RIR values for 2mT (62 nm thick) and 5mT (76 nm thick) from the experimental HAADF images were fitted into the linear equation derived in Fig. 5.10, yielding the corresponding y values,

which represent the defect composition. The evaluated y (Δy) values for 2mT and 5mT were found to be 0.90 (0.04) and 0.92(0.04), respectively.

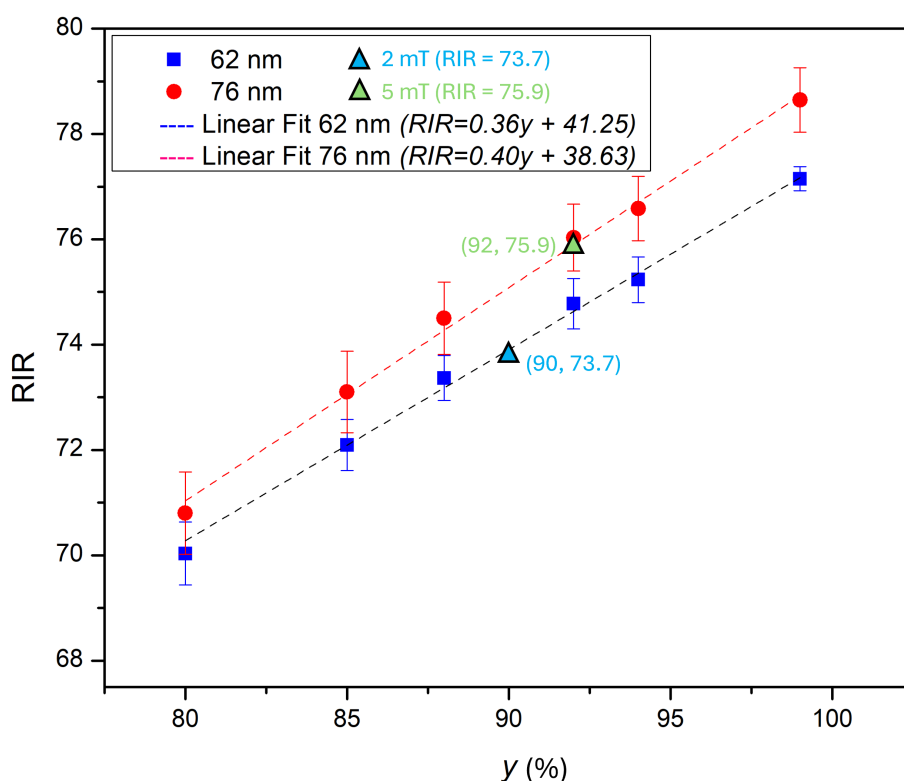


Fig. 5.10 Plot of RIR vs y for the thicknesses of 62 nm and 76 nm by interpolating the data from the Fig. 5.6(a) along with the fit of experimental RIR values of 2mT and 5mT on its corresponding thickness plot of 62 nm and 76 nm respectively.

By correlating y with the B-site composition, it can be determined that the 2mT sample consists of 94.5% Mn and 5.5% La at the B-site. Similarly, for the 5mT sample, the B-site composition is 96% Mn and 4% La. These results are summarised in Table 5.2. Based on these findings, it can be concluded that the sample fabricated under 5mT pressure exhibits a lower concentration of antisite defects compared to the 2mT sample. The observed changes in Mn composition are approximately 1% of the total composition. Under ideal circumstances and with the right adjustments, quantification error in EELS normally falls between 1% and 2%, but it can rise to 10% to 30% or more based on variables like sample thickness,

background subtraction precision, and instrumental parameters like collection angle and alignment [70–73, 69, 74]. Our study demonstrates that the used procedure performs a quantification of antisite defects beyond the standard TEM analytical techniques. This approach facilitates the quantification of antisite defects whenever atomically resolved HAADF images are available and can be applied to similar samples, allowing defect quantification in future studies.

Sample	RIR	Thickness	y (Δy)	B site composition (%)	
				La	Mn
2 mT	73.7	62 nm	0.90 (0.04)	5.5	94.5
5 mT	75.9	76 nm	0.92 (0.04)	4	96

Table 5.2 Quantification of antisite defects of the experimental samples, displaying their RIR, thickness, y values, and B site composition.

5.6 Discussion

This chapter introduces an approach in quantitative defect analysis for advanced oxide materials with a focus on LSMO systems.

The innovation lies in the use of relative HAADF-STEM intensities as a strategy for quantifying antisite defects. By determining the interrelation between RIR, sample thickness, and defect concentration using systematic simulations, we offer a framework that can be applied to other perovskite systems with analogous defect structures. The correlation between growth oxygen partial pressure and antisite defect concentration as observed serves as direct proof that the chemistry of defects is significantly affected by synthesis conditions.

Although the emphasis on $\text{La}_{\text{Mn}}^{\times}$ antisite defects is well founded because they have a majority concentration, the existence of other defect species (vacancies, interstitials) adds some indeterminacy to the interpretation. The hypothesis that other defects have no significant influence on intensity fluctuations might not be universally valid for all synthesis conditions or perovskite compositions.

The need for accurate thickness determination via EELS t/λ measurements increases the analysis workflow complexity but is necessary for reliable quantitation. The relatively homogeneous thickness distributions found in our samples may not be obtainable in all specimen preparation protocols, which could restrict the applicability of the method.

For solid oxide fuel cell applications of LSMO, quantifying antisite defects is critical for ionic conductivity and catalytic optimisation. The phenomenon of synthesis pressure versus defect density offers a clear path for material property tuning via processing parameter control. Application to two distinct samples proves its usefulness, yet more general validation across laboratories and different specimen preparation routes will enhance confidence in the general use of the methodology.

5.7 Conclusions

Overall, the findings of the study can be summarised as the following.

- HAADF-STEM imaging was employed to detect and quantify antisite defects. This technique provides Z-contrast imaging, enabling to measure the change in intensity of the image with respect to effective atomic number in a column.
- HAADF image simulations of LSMO samples for [101] and [001] zone axes were performed with varying defect quantity and sample thicknesses.
- Relative Intensity Ratio (RIR) parameter was evaluated which provided a framework for the analysis of experimental images.
- Experimental HAADF images were analysed using ATOMAP software to measure the RIR. Comparison with simulation data allowed for the quantification of the defect in the experimental sample.
- The developed methodology provides a first-hand approximation for quantifying antisite defects in LSMO, with potential applicability to other perovskite materials.

5.8 References

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Appendix A

Scientific Curriculum

A.1 Education

2021-2025 **PhD Student in Nanoscience Program**, University of Barcelona, Barcelona, Spain.

2019-2021 **Masters in Renewable Energy Science and Technology**, Ecole Polytechnique, Palaiseau, France.

2014-2018 **Bachelor of Technology in Power Engineering**, National Power Training Institute, Durgapur, India.

A.2 Grants awarded

2021-2024 AGAUR FI 2021 Predoctoral Grant awarded by AGAUR. Grant reference: 2021 FI_B 00157.

A.3 Journal publications

Chiabrera, F. M., Baiutti, F., Börgers, J. M., Harrington, G. F., Yedra, L., Liedke, M. O., Kler, J., Nandi, P., Sirvent, J. D. D., Santiso, J., López-Haro, M., Calvino,

J. J., Estradé, S., Butterling, M., Wagner, A., Peiró, F., De Souza, R. A., Tarancón, A. *The impact of Mn nonstoichiometry on the oxygen mass transport properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_y\text{O}_{3\pm\delta}$ thin films*, *Journal of Physics: Energy*, 4 (4), 044011, **2022**. DOI: 10.1088/2515-7655/ac98df.

Gu, R., Xu, R., Delodovici, F., Carcan, B., Khiari, M., Vaudel, G., Juvé, V., Weber, M. C., Poirier, A., Nandi, P., Xu, B., Gusev, V. E., Bellaiche, L., Laulhé, C., Jaouen, N., Manuel, P., Dkhil, B., Paillard, C., Yedra, L., Bouyanfif, H., Ruello, P. *Superorders and terahertz acoustic modes in multiferroic $\text{BiFeO}_3/\text{LaFeO}_3$ superlattices*, *Applied Physics Reviews*, 11 (4), 041415, **2024**. DOI: 10.1063/5.0203076.

A.4 Conference contributions

- Jun 2024** **IN²UB Annual Meeting**, Universitat de Barcelona, Spain. Poster Presentation. Title: *"Investigating vacancies and anisotropic defects using STEM and iDPC imaging techniques"*. Authors: Nandi, P.; Barthel, J.; López-Haro, M.; Calvino, J. J.; Chiabrera, F.; Baiutti, F.; Tarancón, A.; Peiró, F.; Yedra, L.; Estradé, S.
- Sep 2023** **20th International Microscopy Congress**, Busan, Republic of Korea. Poster Presentation. Title: *"Simulation of STEM and iDPC images for developing novel identification and qualitative methods to detect anisotropic defects and vacancies"*. Authors: Nandi, P.; Barthel, J.; López-Haro, Miguel.; J Calvino, J.; Chiabrera, F.; Baiutti, F.; Tarancón, A.; Peiró, F.; Yedra, L.; Estradé, S.
- Sep 2023** **MFS2023**, INL - International Iberian Nanotechnology Laboratory, Braga, Portugal. Oral Presentation. Title: *"Unveiling Vacancies and anisotropic defects in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) through STEM and iDPC simulation imaging"*. Authors: Nandi, P.; Barthel, J.; López-Haro, M.; Calvino, J. J.; Chiabrera, F.; Baiutti, F.; Tarancón, A.; Peiró, F.; Yedra, L.; Estradé, S.
- Jul 2024** **XXIX Reunion bienal de la Real Sociedad Española de física**, Donosti, Espanya. Oral Presentation. Title: *"Novel TEM tools to shed light into ASSB"*

cathode materials". Authors: Yedra, L.; Nandi, P.; Vargas B.; del-Pozo-Bueno, D.; Plana-Ruiz, S.; Monteiro Freitas, F.; González-Rosillo, J.C.; Morata, A.; Estradé, S.; Peiró,.

Jun 2024 **XVII Congreso nacional de materiales CNMAT 2024**, Malaga, Espanya. Oral Presentation. Title: *"Una nueva visión nanoscópica sobre los materiales de cátodo de las ASSB"*. Authors: Yedra, L.; Nandi, P.; Vargas B.; del-Pozo-Bueno, D.; Plana-Ruiz, S.; Monteiro Freitas, F.; González-Rosillo, J.C.; Morata, A.; Estradé, S.; Peiró,.

Sep 2023 **Microscopy at the Frontiers of Science 2023**, Braga, Portugal. Oral Presentation. Title: *"Unveiling the Optical Response Characteristics of HfO₂ Thin Layers with Different Phases via EELS Analysis"*. Authors: Vargas, B.; Nasiou, D.; Molina-Luna, L.; Coll, C.; del Pozo Bueno, D.; Nandi, P.; Estradé, S.; Yedra, Ll.; Kaiser, N.; Alff, L.; López-Conesa, Ll.

Sep 2023 **Microscopy at the Frontiers of Science 2023**, Braga, Portugal. Oral Presentation. Title: *"Measurement of local dielectric function of HfO₂ Thin Layer with different crystallographic phases from EELS Analysis."*. Authors: Vargas, B.; Nasiou, D.; Molina-Luna, L.; Coll, C.; Del Pozo Bueno, D.; Nandi, P.; Yedra, L.; Kaiser, N.; Alff, L.; López-Conesa, L.; Peiró, F.

Sep 2023 **20th International Microscopy Congress**, Busan, Republic of Korea. Oral Presentation. Title: *"The defects behind fast ionic transport pathways in thin layers: An atomic exploration of LaSrMnO₃"*. Authors: Yedra, L.; Nandi, P.; Blanco-Portals, J.; López-Conesa, L.; Martín, G.; Ruiz-Caridad, A.; Baiutti, F.; Chiabrera, F.; Diercks, D.; Cavallaro, A.; Ga.

Sep 2023 **20th International Microscopy Congress**, Busan, Republic of Korea. Poster Presentation. Title: *"Dielectric function and electron energy loss function of HfO₂ thin layers with hexagonal and rhombohedral phases by using EELS."*

Authors: Vargas, B.; Nasiou, D.; Molina-Luna, L.; Coll, C.; Del Pozo Bueno, D.; Nandi, P.; Yedra, L.; Kaiser, N.; Alff, L.; López-Conesa, L.; Peiró, F.

A.5 Workshops and Schools

- Feb 2022** **European Universities Community (EUC)**, Strasbourg, France. European Students' Assembly to contribute to shaping the future of Europe from a student perspective.
- May 2022** **Safety Workshop (Prevenió de Riscos Laborals al Laboratori)**, University of Barcelona, Spain
- May 2022** **Quantitative Electron Microscopy (QEM)**, Le Barcarès, France. Workshop on quantitative methods in scanning and transmission electron microscopy.
- Sep 2022** **TEM-UCA European Summer Workshop**, University of Cadiz, Spain. School in Scanning and Transmission Electron Microscopy of Nanomaterials.
- Oct 2023** **CECAM Flagship School: "First steps with SIESTA: from zero to hero"**, www.siesta-project.org/siesta/events/SIESTA_School-2023.
- Apr 2024** **WIEN2k Hands-On Workshop for New and Existing Users**, ICTP, Trieste, Italy. Participated in and presented a poster at the workshop.
- Jul 2024** **73rd Lindau Nobel Laureate Meeting**, Lindau, Germany.

A.6 Supervision of research projects

Co-supervision of Bachelor Thesis, *"An experimental and simulation-based approach for a $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$ (LSMO) characterization"* by Ona Falcó Artero, Bachelor's degree in Physics, University of Barcelona. Dates: Spring semester, 2023/2024.

Co-supervision of Master Thesis, *"Synthesis and Characterization of $\text{CoFe}_2\text{O}_4@ \text{NiO}$ Core@Shell Bimagnetic Nanoparticles"* by María José González Aréchiga Dorazco, Erasmus Mundus Master of Science in Nanoscience and Nanotechnology, Katholieke Universiteit Leuven. Academic year 2023–2024.

A.7 Teaching activities

Autumn 2022/2023 Informatics (Technical Practicum), Bachelor's in Electronic Engineering of Telecommunications, 26 hours. Dates: Autumn semester, 2023/2024.

Autumn 2023/2024 Informatics (Technical Practicum), Bachelor's in Biomedical Engineering, 26 hours. Dates: Autumn semester, 2023/2024.

A.8 Dissemination activities

Apr 2022 Festival 10alamos9. *Website:* <https://10alamos9.es/>. Dates: April 26-27, 2022.

May 2022 Festa de la Ciència at the Universitat de Barcelona. *Website:* <http://www.ub.edu/laubdivulga/festacienciaub/escoles.html>. Dates: May 27-28, 2022.

May 2023 Festa de la Ciència at the Universitat de Barcelona. *Website:* <http://www.ub.edu/laubdivulga/festacienciaub/escoles.html>. Dates: May 12-13, 2023.

May 2024 Festa de la Ciència at the Universitat de Barcelona. *Website:* <http://www.ub.edu/laubdivulga/festacienciaub/escoles.html>. Dates: May 10-11, 2024.

Appendix B

Resum en Català

B.1 Paraules clau

Microscòpia Electrònica de Transmissió (TEM)

Microscòpia Electrònica de Transmissió d'Escaneig (STEM)

Camp Fosc Annular d'Alt Angle (HAADF)

Espectroscòpia de Pèrdua d'Energia d'Electrons (EELS)

Estructura de la Vora de Pèrdua d'Energia (ELNES)

Teoria del Funcional de la Densitat (DFT)

Simulació Multiescala

Simulació d'Imatge STEM

Funció Dielèctrica

Defectes Antisite

ATOMAP

Simulació EELS

B.2 Títol

Anàlisi quantitativa multimodal de materials funcionals: Simulació EELS STEM i DFT.

B.3 Resum

Aquesta tesi examina les propietats a nivell atòmic de materials complexos mitjançant simulacions avançades i microscòpia electrònica d'alta resolució. L'estudi utilitza la microscòpia electrònica de transmissió de rastreig (STEM), l'espectroscòpia de pèrdua d'energia dels electrons (EELS) i la teoria del funcional de la densitat (DFT) per aprendre més sobre la química dels defectes, les fases estructurals i com es comporten els electrons en diferents materials. La motivació i els objectius de la tesi es descriuen al capítol 1.

El capítol 2 parla de les idees bàsiques darrere de l'anàlisi d'imatges STEM i la simulació d'imatges i DFT-EELS. Explica com obtenir dades quantitatives a partir d'imatges de resolució atòmica mitjançant eines de programari com Atomap. El mètode multislice de simulació d'imatges s'explica en detall com una manera de modelar com les ones d'electrons es mouen a través d'estructures cristal·lines. El capítol també parla de les simulacions EELS basades en DFT, que utilitzen la densitat electrònica, les funcions dielèctriques i els espectres de pèrdua d'energia per ajudar-nos a comprendre les característiques de baixes pèrdues i pèrdues profundes que es veuen en els espectres experimentals.

El capítol 3 estudia els detalls sobre els dispositius de memòria d'accés aleatori resistiu (RRAM) basats en HfO_2 , amb un enfocament en com les vacants d'oxigen canvien les propietats electròniques d'aquests dispositius. S'utilitzen simulacions DFT per modelar la funció dielèctrica i els espectres EELS per a diferents estequiometries i fases estructurals. Els resultats simulats ajuden a explicar els canvis en els espectres experimentals i mostren com les vacants d'oxigen afecten la resposta dielèctrica.

Al capítol 4, examinem els cluster de gas xenó continguts en làmines de grafè i com la pressió i l'estat de càrrega afecten els espectres EELS obtinguts. Els espectres EELS experimentals mostren canvis consistents en les posicions i formes dels pics. Això condueix

a simulacions DFT-EELS de cúmuls de xenó amb diferents nivells d'ionització i confinament de càrrega.

La mesura de defectes en $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) mitjançant imatges i simulació HAADF-STEM és el tema principal del capítol 5. Els àtoms de La creen defectes ocupant llocs de Mn en aquest òxid de perovskita, i això té impacte en el contrast de les imatges HAADF. Es desenvolupa una tècnica d'anàlisi basada en una relació d'intensitat relativa utilitzant Atomap després d'executar diverses simulacions d'imatges per a diferents concentracions de defectes. Les densitats de defectes es calculen analitzant i comparant simulacions amb imatges experimentals HAADF de mostres de LSMO crescudes a diferents pressions d'oxigen. L'estudi presenta un protocol per quantificar defectes en capes primes de LSMO.

En conclusió, la tesi millora la comprensió de la caracterització de diversos materials per tècniques de microscòpia electrònica mitjançant diversos tipus de simulacions.

Appendix C

Resum en Anglès

This thesis looks into the atomic-level properties of materials by using advanced simulations and high-resolution electron microscopy. The study uses Scanning Transmission Electron Microscopy (STEM), Electron Energy Loss Spectroscopy (EELS), and Density Functional Theory (DFT) to learn more about defect chemistry, structural phases, and how electrons behave in different materials. The motivation and objectives of the thesis are described in Chapter 1.

Chapter 2 talks about the basic ideas behind STEM image analysis and Image and DFT-EELS simulation. It explains how to get quantitative data from atomic-resolution images using software tools like Atomap. The multislice method of image simulation is explained in detail as a way to model how electron waves move through crystal structures. The chapter also discusses DFT-based EELS simulations, which use electronic density, dielectric functions, and energy loss spectra to help us understand both low-loss and core-loss features seen in experimental spectra.

Chapter 3 studies the details about HfO₂-based resistive random-access memory (RRAM) devices, with a focus on how oxygen vacancies change the electronic properties of these devices. We used DFT simulations to model the dielectric function and EELS spectra for different stoichiometries and structural phases. The simulated results helped explain changes in the experimental spectra and showed how oxygen vacancies affect the dielectric response.

In Chapter 4, we look at embedded xenon gas clusters and how pressure and charge state affect their EELS behaviour. Experimental EELS spectra showed consistent changes in the positions and shapes of peaks. This led to DFT-EELS simulations of xenon clusters with different levels of ionisation and charge confinement, leading to a deeper understanding of material behaviour.

The measurement of antisite defects in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSMO) through HAADF-STEM imaging and simulation is the main topic of Chapter 5. La atoms create defects by occupying Mn sites in this perovskite oxide, influencing the HAADF characteristics. A new analysis technique based on a Relative Intensity Ratio (RIR) was created using *Atomap* after several image simulations were run for varying degrees of antisite defects. Defect densities were calculated by analysing and comparing simulations with experimental HAADF images of LSMO samples grown at different oxygen pressures. The study presents an approach to quantifying defects in LSMO thin films.

In conclusion, the thesis has increased the understanding of the electron microscopy characterisation of several materials through the use of various simulations.