1. Publishable Summary

Current research and industrial attention on functional oxide materials is based on their wide range of applications including memory devices, spintronics, fuel cells, and solar cells. The functional properties of these complex oxide systems, and thus the performance of their applications, lie on the active surfaces, when nanoparticles are involved, or the active interface, when the focus is placed on thin films. The EPOFO (Electron Probing Of Functional Oxides) project's aim was to relate the structural and chemical character of the popular nanoscale functional oxide materials to their functional property (whether this is electric, magnetic, or catalytic), and thus to their performance. The wide applications of these materials have triggered intense research towards the better understanding of the physical and chemical issues that govern the functionality of nanoscale particles, or thin films in devices and the demand for the development and applications of characterization methods that are able to probe the physicochemical materials parameters on the very local scale, or even to manipulate them, becomes prominent.

Herein, the focus was to thoroughly and unambiguously characterize the surfaces and interfaces that are responsible for their functional properties. This way, their performance can be predicted and tuned in order to bring these materials on the next-generation technological and application state as a reliable, better, and cheaper product. Towards this end, an integrated multidisciplinary approach engaging materials science, nanoscale science, physics, as well as physical chemistry was undertaken. State-of-art nanoanalytical electron microscopy techniques were applied and developed. Specifically, the research objectives of the proposal were:

(i)   To investigate the structural defects of functional oxide interfaces in thin film configurations of devices
(ii) To probe the chemistry at the interface and surfaces of these materials
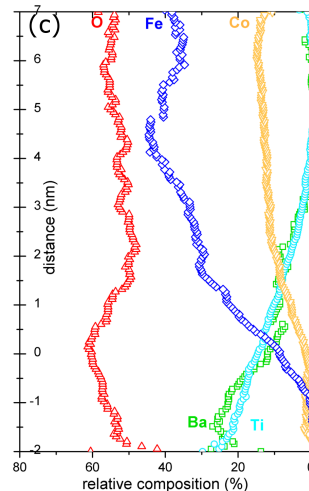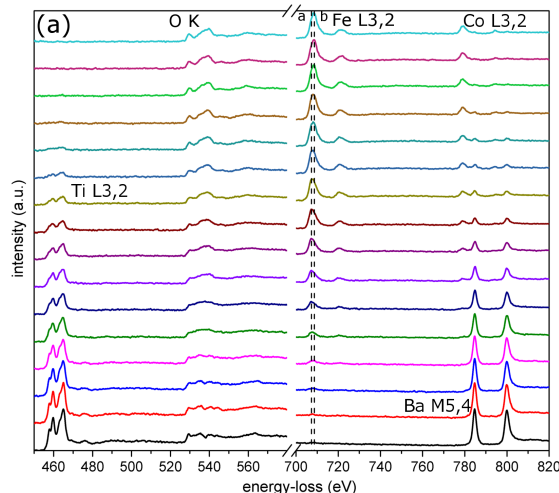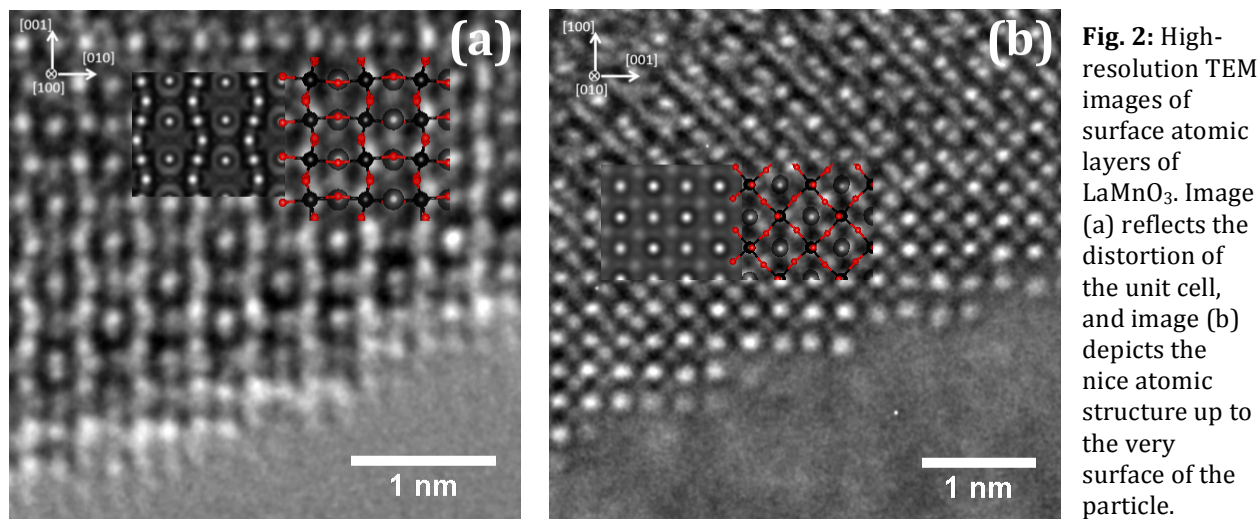(iii) To evaluate space charge distributions that could inhibit the functional properties at the interfaces/surfaces

Fig.1: (a) EEL spectra of the O K and Fe $L_{3,2}$ edges and (b) a corresponding annular dark field (ADF) image showing the evolution of the thin film structure. The beginning of the interface is defined at 0. (c) Calculated relative compositional profiles for all elements in the system indicating the extensive, disparate character of the interface.

Our findings reveal for the first time on an atom-by-atom scale the chemical complexity of the heteroepitaxy between $CoFe_2O_4$ and $BaTiO_3$ along the (001) crystallographic direction.

The inherent polarity of the substrate results in surface strain at both sides of the interface. The adopted, highly disordered interfacial structure is ~2 nm thick and it is non-stoichiometric. Quantitative analysis uncovered an different phase (ilmenite) structure as the immediate interfacial layer (see chemical intermixing of the thin film structure in Fig.1). The results provide structural and chemical evidence of the incompatibility of the ferroelectric $BaTiO_3$ with the ferrimagnetic $CoFe_2O_4$. Ultimately, the failure to control the quality at the interface impedes the elastic strain effects required for the strong magnetoelectric coupling of the composite system. However, for this functional oxide system, the results corroborate a chemical activity between these two oxides that could lead to synthesis of complex engineered interfaces.

The catalytic functionality of nanoparticles is directly linked to the active surface sites taking part in the reaction. Oxide perovskite-type catalysts exhibit exceptional catalytic performance and are the best contender in replacing the conventional, costly, metal catalysts. At the moment, their applicability is hindered due to the little knowledge of the actual mechanisms by which the reactions proceed. First, we evaluated the surfaces by transmission electron microscopy (TEM) where the perfect structure up to the surface was revealed (Figure 2). Next, we probed the surface and subsurface of a working perovskite catalyst, $LaMnO3$, by electron energy-loss spectroscopy. The extracted experimental information was analyzed utilizing density functional theory calculations and the results reveal that the surface is different than the bulk and the difference consists of both changes in oxidation state and in the number of neighbors (coordination). Previously, all literature concluded rather tacitly that the variation is a simple change in oxidation state.

Fig. 2: High-resolution TEM images of surface atomic layers of $LaMnO_3$. Image (a) reflects the distortion of the unit cell, and image (b) depicts the nice atomic structure up to the very surface of the particle.

To conclude, the EPOFO project thoroughly evaluated the ability of TEM techniques to answer technological important issues that govern the performance of functional oxide nanoparticle systems and thin film heterostructures. During this project, we have thoroughly analyzed the TEM data with the help of theoretical calculations to include effects in the interpretation that were previously omitted. This way, predictions of future engineered oxide structures can be optimized towards the functional oxide structures' successful implementation in working devices.