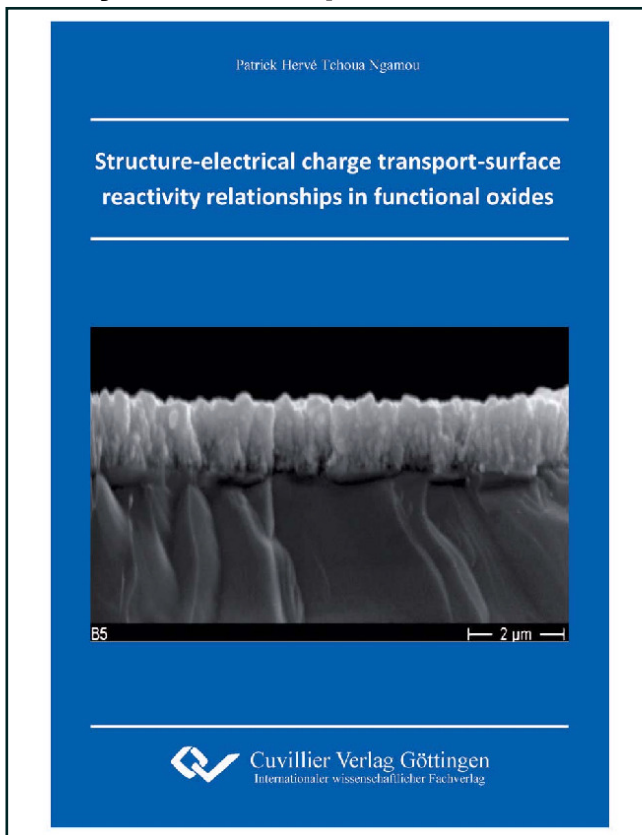




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**Structure-electrical charge transport-surface  
reactivity relationships in functional oxides**



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# 1 Introduction

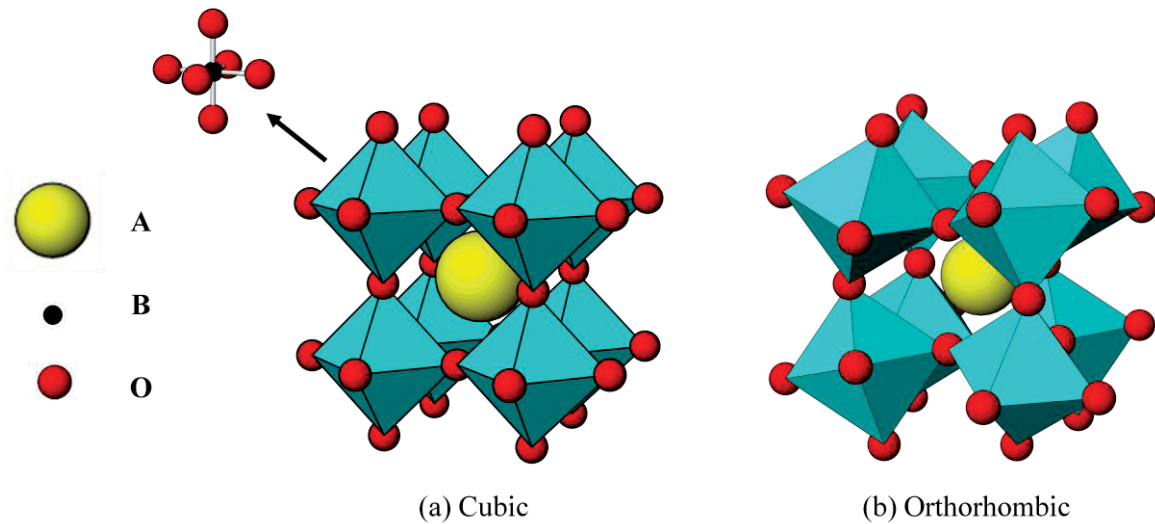
Functional oxides with perovskite and spinel structures have gained considerable interest due to their wide range of industrial applications. Their exceptional physicochemical properties such as gas sensing, semiconducting, oxygen-ion conductivity, electronic, electro-catalytic, catalytic, and magnetic properties have led to intensive research. Furthermore, the high defect tolerance of these structures makes them suitable materials for the chemical engineering to tailor the physicochemical properties for specific applications.

The perovskite structure with general formula  $ABO_3$  is a flexible structure which can almost accommodate all the elements of the periodic table [1]. It consists of vertex-sharing  $BO_6$  octahedra with the A cations located in the 12-fold coordination sites between these octahedra (Figure 1.1). The size of the A and B cations does not necessarily perfectly fit to the sites generated by the structure. As a result, the structure is easily distorted from the ideal cubic symmetry to lower symmetries depending on the elements present. The Goldschmidt factor tolerance ( $t$ ) is often used to predict whether a compound will form the perovskite structure and it is given by [2]:

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}$$

Where,  $R_A$ ,  $R_B$  and  $R_O$  are the relative ionic radii of the A site and B site cation and the oxygen anion respectively.

The perovskite structure is stable for  $0.78 < t \leq 1$  and a tolerance factor close to the unity is generally observed for the ideal cubic structure because of the good matching of the ionic sizes. The structure distorts to accommodate smaller A cations when the tolerance factor satisfies  $0.78 < t < 1$ . The distortion is generally due to the  $BO_6$  tilting such that the B-O-B angle bonds are no longer equals to  $180^\circ$ , which reduces the symmetry of the structure [3].



**Figure 1.1: Perovskite distortion from (a) cubic to (b) orthorhombic.**

Several authors have demonstrated the intimate relation between the crystal structure and various physical properties, these structural distortions often result in variations in the physical properties. For example, Torrance et al. [4] have observed a correlation between the degree of the  $\text{BO}_6$  tilting and the temperature at which the insulator-to-metal transition occurs in  $\text{ANiO}_3$  ( $A = \text{Eu, Sm, Nd, Pr}$ ) perovskites. Furthermore, Yamaguchi et al. [5] have investigated the  $\text{ACoO}_3$  ( $A = \text{Eu, Sm, Nd, Pr, La}$ ) perovskites and correlated the optical and electrical properties with the degree of distortion. The partial substitution of La or Nd by a divalent Sr cation in  $\text{LaCoO}_3$  or  $\text{NdNiO}_3$  perovskites was found to highly enhance the electrical conductivity due to a charge compensation effect which induces the formation of holes ( $\text{Co}^{4+}$  or  $\text{Ni}^{4+}$ ) and shifts the insulator-to-metal transition towards low temperatures [6, 7]. The investigation of the insulator-to-metal transition near the Fermi level using electron-spectroscopy [8], has shown that the electronic structure of the transition metal B of perovskite oxides has its frontier  $d$ -orbitals close in energy to the  $\text{O}(2p)$  orbitals. The overlap of the  $p$ - $d$  orbitals was identified as the cause of the insulator-metal transition, in agreement with the *ab-initio* calculations of the electrical structure of  $\text{LaCoO}_3$  and  $\text{La}(\text{Sr})\text{CoO}_3$  [9, 10].

The effect of the crystal structure on the catalytic properties of pure and Sr-doped ANiO<sub>3</sub> towards the oxidation of CO was investigated by Falcon et al. [11]. These authors have shown that the catalytic activity increases with the tolerance factor. The same conclusion was drawn by Arakawa et al. [12] upon the study of the oxidation of methanol over Sm<sub>0.5</sub>A<sub>0.5</sub>CoO<sub>3</sub>.

Recently, Chang et al [13] has noticed that 10 mole % strontium inserted in LaCoO<sub>3</sub> achieved higher NO to NO<sub>2</sub> conversions than the commercial platinum-based catalyst. In fact, a computational modelling study has shown that during the substitution of La by Sr in LaCoO<sub>3</sub>, relative to the bulk, the formation of oxygen vacancies at the surface of the catalyst is energetically more favorable [14]. Bialobok et al. [15] have experimentally shown that this substitution increased the basic character of the perovskite.

Such correlations clearly show that the electronic structure of perovskites dictates their electrical properties and plays a major role in determining their surface reactivity. However, all these investigations were made on different type of materials. Generally, single crystals were used for the investigation of the structure-electrical properties relationships, while the powder is typically used for the study of the structure-reactivity interplay. In this work, PSE-CVD was used as a rational and reliable method for the controlled-growth of polycrystalline spinel and perovskite oxides as thin films to bridge the material gap in the investigation of the interplay between the crystal structure, electrical charge transport, optical properties and surface reactivity. Furthermore, the adopted synthesis method was used to intentionally alter the structure to a large extent using doping strategy.

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## 2 Experimental method and techniques

*Several complementary characterization techniques were necessary to carry out the research work described in this thesis. The present chapter is dedicated first to the general description of the Pulsed-spray evaporation CVD technique which was employed to grow single phase of spinel and perovskite oxide films. Next, the analytical techniques used to probe the structural, electrical and catalytic properties are described and briefly discussed.*

The continuous increasing demand on the performance of thin film device forces the improvement of the quality of existing materials and the development of new ones. Achieving these goals entails the development of new or controlled deposition processes enabling the growth of materials with improved quality at reduced costs. To fulfill these requirements, pulsed-spray evaporation CVD was used in this thesis as a method of choice for the growth of functional oxides with spinel and perovskite structures. Furthermore, complementary characterization techniques were employed to understand the relationship between the growth, the structure and the final film properties. The characterization techniques used in this thesis can be regrouped in two categories. The first characterization category includes X-ray diffraction (XRD), energy dispersive x-ray (EDX), scanning electron microscopy (SEM) and the Raman spectroscopy. The second type of characterization concerns the physico-chemical properties such as the electrical transport and surface reactivity measurements.

### 2.1 Chemical vapor deposition of oxide films

Chemical vapor deposition (CVD) is a film growth technique in which a chemical reaction of gaseous species takes place on or near a substrate surface and produces a solid material which forms the film. The reaction gaseous-products are evacuated from the deposition zone by a gas flux. Generally, reactive precursors with high vapor pressure are necessary for a chemical reaction to occur spontaneously on the substrate surface. In conventional CVD, a thermal

energy is used to activate the chemical reaction and the pressure may vary from atmospheric pressure to low pressure [1]. Nevertheless, the CVD reaction can be initiated by different energy sources which gives rise to several CVD variants such as plasma enhanced CVD (PECVD) [2], photo-assisted CVD (PACVD) [3] and flame-assisted CVD (FACVD) [4]. Unlike physical deposition methods, CVD techniques have been shown to be highly efficient for coating large surfaces and complex- shape objects [5].

Among the CVD techniques, metalorganic CVD (MOCVD) [6] has been classified as a variant of CVD in which metalorganic compounds are used as precursors. The advantage of MOCVD is the possibility to deposit at relatively low temperatures. Furthermore, most elements in the periodic table possess commercially available volatile metalorganic compounds. MOCVD is conventionally associated with bubbler evaporation, where the main drawback resides in the difficulty to grow multicomponent materials with well controlled stoichiometry using multi-source precursors because of the inherent difference in the vaporization rate of various precursors. This difficulty has been surmounted by the development of liquid delivery processes such as aerosol-assisted CVD [7].

Pulsed spray evaporation CVD (PSE-CVD) is a liquid delivery process which consists of a pulsed injection of a precursor-containing liquid feedstock into an evaporation zone using a high-speed electro-valve. The injection rate of the liquid feedstock is controlled by adjusting the valve opening time (2.5-40 ms) and the injection frequency (2-100Hz). The liquid delivery presents several advantages:

- The film thickness, the stoichiometry and the growth rate can be easily controlled by adjusting the relative precursor concentrations in the liquid feedstock, the injection frequency and the opening time of the electro-valve which act on the precursor flux [8].

- Several injectors with different liquid feedstocks can be used to obtain multilayers or superlattices [9, 10].
- A reproducibility of the growth is relatively easily obtained since the liquid feedstock is maintained at room temperature where no significant thermal degradation takes place.

The deposition was performed in a home-made vertical cold-wall type reactor as schematically shown in Figure 2.1. The upper side of the reactor is equipped with a pulsed-spray evaporation (PSE) system for the delivery of liquid precursor feedstocks. Metal acetylacetonate precursors, purchased from Strem Chemical, were dissolved in ethanol with desired ratio and kept at room temperature under atmospheric pressure during the deposition. Acetylacetonate complexes were selected as precursors owing to their stability and high solubility in ethanol. Furthermore, the availability of these complexes for most metal enables their mixing in single feedstock without disadvantages caused by ligand exchange reactions. The optimal use of the PSE delivery was achieved with a valve opening time of 2.5 ms and a frequency of 4-10 Hz. The evaporation of the injected feedstock takes place under vacuum at 220°C in the tubular 30 cm-long evaporation zone which is heated with an external electric heater. The resulting vapor is transported to the deposition zone with N<sub>2</sub>/O<sub>2</sub> flow rates of 0.5/1 slm. The reaction zone comprises a flat resistive heater perpendicular to the gas flow direction and the substrate temperature was measured by a thermocouple located on its surface. The total pressure inside the reactor is kept at 30 mbar during the deposition. The temperatures for the evaporation and reaction zones, the flow rates of N<sub>2</sub> and O<sub>2</sub>, the position of the substrates and the overall pressure inside the reactor were optimized to attain uniform films with high growth rates.