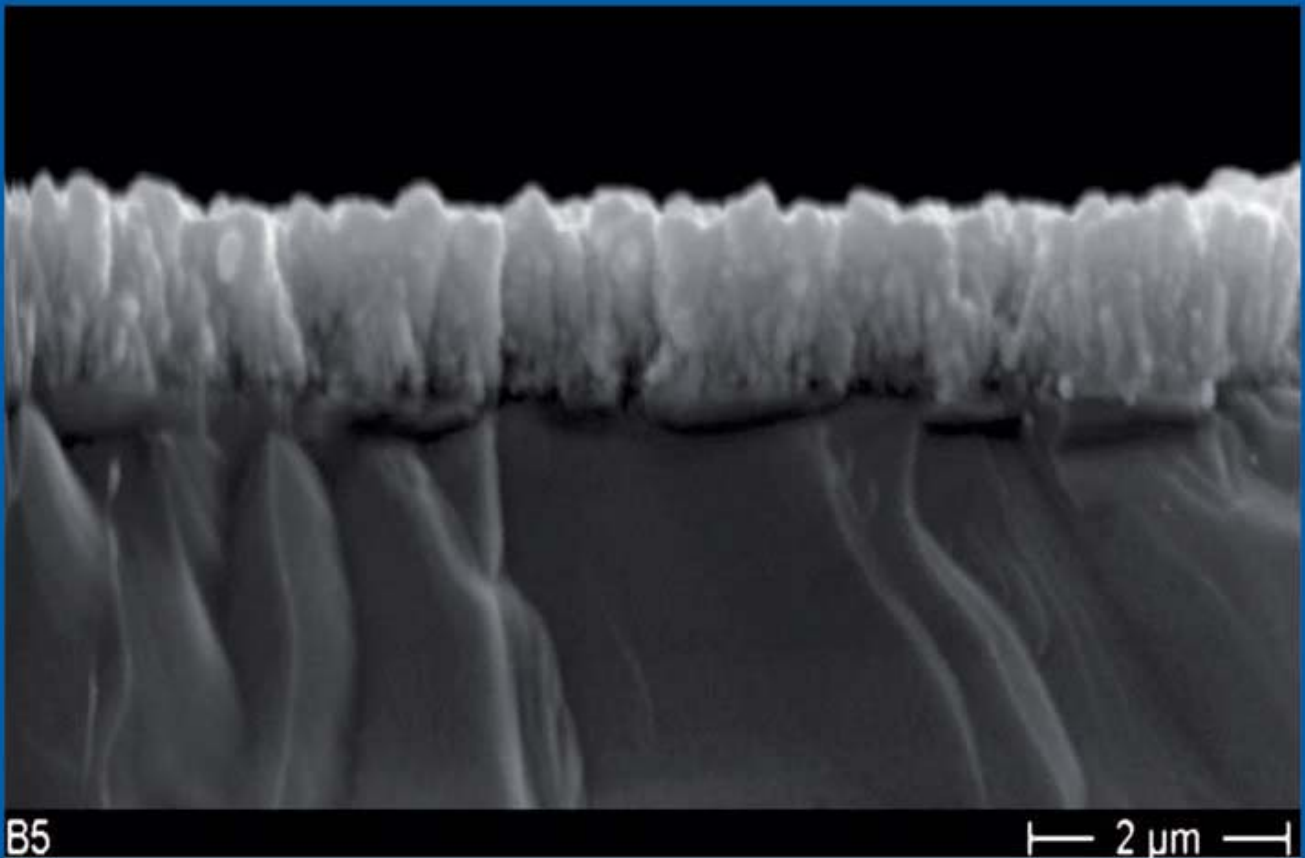


Patrick Hervé Tchoua Ngamou

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



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

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..... *To the dearest memory of my father Mr. Emmanuel Ngamou*

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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° , which reduces the symmetry of the structure [3].