Influence of crystal structure on thermodynamics of proton transport in perovskite materials

Triple conducting oxides (TCOs) are a fascinating group of materials Due to their ability to **conduct three mobile charge carriers** – electrons/holes, oxygen ions, and protons, they are gaining much interest in various scientific areas due to their potential application in electrochemical devices, such as membranes for hydrogen separation or electrodes for protonic ceramic electrochemical devices (PCECs), which are a promising alternative to the popular solid oxide cells with oxygen ion-conducting electrolyte (SOCs). PCECs can bring a variety of advantages, such as longer lifetimes of devices, less degradation, and lower costs. In principle, proton ceramics offer a better performance at lower temperatures than conventional oxide ion conductors.

The aim of this project is to determine the relationship between the crystal structure and proton transport in selected groups of perovskite materials (general chemical formula ABX_3) exhibiting mixed ionic-electronic conductivity (MIEC). The materials selected for the studies are perovskite-based TCOs, which can be divided into two groups: materials with much lower ionic conductivity than the electronic ($t_{el}\approx1$) and materials with low electronic conductivity and predominant oxygen ion conductivity ($t_{ion}\approx1$). The first group of investigated materials is $SrFe_{1-x}Co_xO_{3-\delta}$ (for x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.8) and $Ba_xSr_{1-x}Ti_{1-y}Fe_yO_{3-\delta}$ (for x = 0.5 and y = 0.6 - 0.8) compounds, while the second group is related to the doped barium cerate-zirconate solid solution: $Ba_{0.6}Ce_{0.2}Zr_{0.2}Y_{0.1}M_{0.1}O_{3-\delta}$ (where M = Tb, Pr, Fe).

To introduce protons into the TCO material, it has to be exposed to the humidified atmosphere. Depending on the defect chemistry in different thermodynamic conditions (dominating concentration of vacancies or electron holes), the material can uptake water by undergoing different processes, consuming either vacancies or electron holes. However, the **concentration of protons in the material depends also on its crystal structure and the ions in the unit cell** (fig. 1a). Recent studies have shown that **one of the factors strongly influencing the process of water uptake is the tilting of oxygen-metal-oxygen bonds** in the perovskite unit cell (fig. 1b). To investigate such processes, X-ray diffractometry (XRD) and various spectroscopic methods will be employed. XRD enables to determine the overall crystal structure of the sample and its phase purity (is there only one type of material present or more). Spectroscopic studies using X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Fine Structure (XAFS) methods can bring valuable information about the oxidation state of transition metals in the compounds and the local arrangement of the atoms in the unit cell, allowing the determination of the angle α between the bonds presented in fig. 1b.

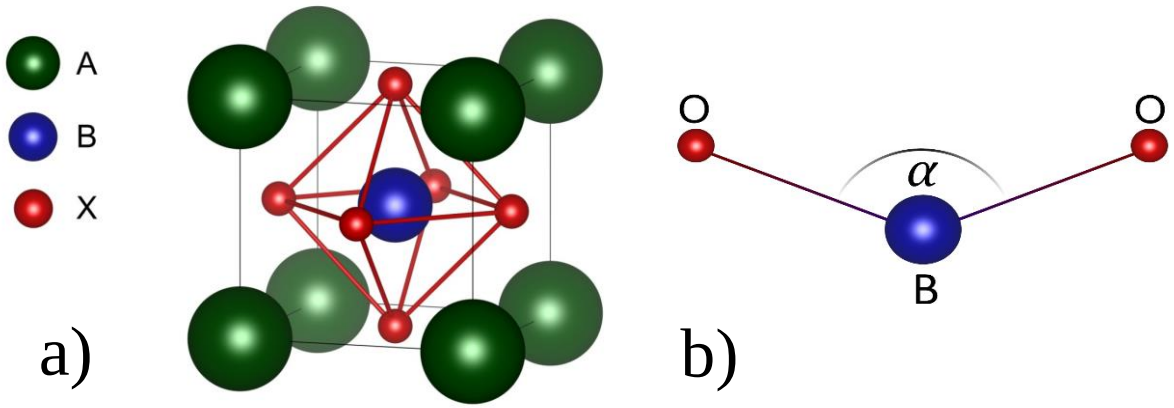

Fig. 1. a) Unit cell of ideal cubic perovskite (ABX_3); b) Tilted bonds between cation B and oxygen ions (X - oxygen)

To analyse the water uptake processes in the investigated oxides, they will be studied using thermogravimetry (TG) method, which enables to determine the concentration of protons and hydration enthalpies in the materials by observing the change of samples' mass as a function of temperature. An important part of the project will be to investigate the electrical transport properties of the materials using DC and AC techniques. One of the most important methods will be Electrical Conductivity Relaxation (ECR), which allows to determine the transport parameters such as migration enthalpy, diffusion coefficients, and mobility of protons in the structure, which makes it a pivotal tool in studying the electrical and thermodynamic parameters of TCOs.

Several factors, like the **electron affinity of the chemical species present in materials, the structure distortions as well as a covalence of transition metal–oxygen bonds may play a major role in analysing and explaining water uptake in TCOs**.