X-ray absorption as a potent tool in studies of proton-conducting cobalt-based perovskites

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Double perovskite cobaltites with the general formula $BaLnLn'Co_2O_{6-\delta}$, (where Ln, Ln' = La, Nd, Pr, Sm, Gd, Dy, Tb) are a widely studied group of material, that results from their application potential[1,2]. Materials from this group exhibit high mixed electron-ion conductivity[3]. Some selected compositions are also reported with a minor partial on proton conductivity[3], which opens the possibility of using these compounds as cathode materials in proton ceramic fuel cells (PCFC)[4]. Proton conductivity is possible if the material can incorporate water into its structure.

Properties of $BaLnLn'Co_2O_{6-\delta}$ may be tailored due to the transitional nature of cobalt. It may exhibit different oxidation and spin states, which affects the oxygen stoichiometry and electronic structure of the material. This, on the one hand, may be very beneficial, but on the other is very challenging because to fully understand the properties of the materials from this group a full description of oxidation and spin state is necessary. Especially, the investigation of the spin state is difficult and requires the use of sophisticated research techniques, like synchrotron studies.

The structure of $BaLnLn'Co_2O_{6-\delta}$ was studied by the means of combined synchrotron radiation X-ray diffraction, and neutron powder diffraction, iodometric titration was used to determine the cobalt oxidation state at room temperature, while soft X-ray absorption spectroscopy was used to investigate the spin state of cobalt spectroscopy (measurement performed at the O K-edge and Co L_{23}-edges at the temperature range from 80 K – RT). The methods used allowed to determine the relations between cobalt oxidation and spin state and ionic radius of lanthanide, as well as temperature.

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