

XAFS STUDY AND CRYSTALLOGRAPHIC STRUCTURE OF Ti AND Y DOPED BaCeO_{3-δ} PROTONIC CONDUCTORS

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We report on the XAFS and XRD study of the titanium and yttrium doping influence on the evolution of the crystal structure of a new class of solid electrolytes, Ba(Ce_{1-x}Ti_x)_(1-y)Y_yO_{3-δ} (0 ≤ x ≤ 0.3, 0 ≤ y ≤ 0.1) [1-3].

The compounds studied belong to the family of protonic conductive perovskites, which have potential applications in intermediate temperature fuel cells [4]. The undoped barium cerate is orthorhombic, while the increasing content of Ti dopant up to x = 0.2 leads to a tetragonal or even cubic structure. In the case of Y dopant an increase of ionic conductivity, which is desirable for applications, was observed. The long-term stability of barium cerate in atmospheres containing CO₂ can be improved by titanium addition, while the introduction of yttrium has the opposite effect.

In the present study the local ionic arrangement around the Ti, Y and Ce cations has been studied by means of X-ray absorption spectroscopy in the XANES (X-ray Absorption Near Edge Structure) region and in the EXAFS (Extended X-ray Absorption Fine Structure) region, and compared to the X-ray diffraction results.

The XANES spectra of BaCe_{1-x}Ti_xO₃ at the Ti K-edge show that up to x = 0.2 Ti occupies octahedral B sites in the perovskite structure with a gradual decrease of the symmetry of the environment of the Ti site. The doping at x = 0.3 corresponds to a symmetry of the Ti site possibly close to tetrahedral.

The XAFS spectra at the Ti K and Ce L₂ edges were collected in the transmission mode at ambient conditions at the X and A1 stations, while Y K-edge spectra were measured at room temperature (RT) and 10 K, using K_α PFY (partial fluorescence yield) at the CEMO beamline of the HASYLAB/DESY synchrotron facility and at the ID26 beamline of the ESRF laboratory.

The cerium EXAFS spectra of the Ba_{1-y}Ce_{1-x}Y_xO₃ series show that a larger amount of oxygen vacancies is created by Y doping than by Ba understoichiometry. The yttrium EXAFS reveals a possible location of some Y ions at the Ba sites. The dynamic Debye-Waller effect is

slightly stronger for the Ba stoichiometric sample than for the understoichiometric one.

The cerium EXAFS spectra were simulated for the first coordination shell in BaCeO_{3-δ} (Fig. 1), using FEFF code.

The results are discussed and compared to the electrical transport properties of the materials.

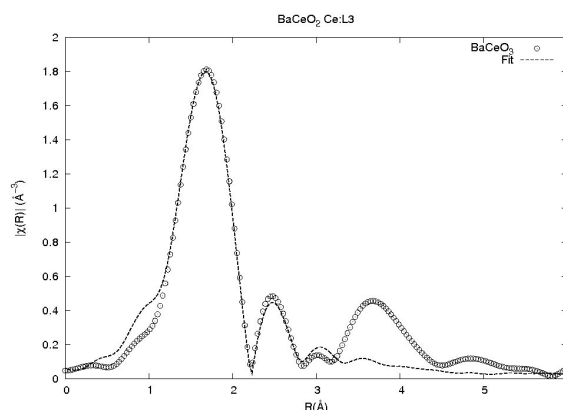


Figure 1. An example of the FEFF fit of the cerium first coordination shell in the *Pnma* structure.

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