

Local atomic structure evolution around dopant ions in YSZ+Mn solid solution

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Yttria stabilized zirconia (YSZ) is a popular material for electrolyte in Solid Oxide Fuel Cells (SOFCs). Aliovalent doping of ZrO₂ with cations that have oxidation state lower than IV generates oxygen vacancies in the material and significantly increases ionic conductivity (naturally occurring in this material at high temperature) so that its magnitude is reasonable for real life applications. Oxygen vacancies are necessary for stabilizing cubic fluorite structure of ZrO₂ and to prevent material from destruction during SOFC operation. Globally, up to solubility limit, the right amount of dopants introduced to ZrO₂ forms solid solution, however locally increased density of oxygen vacancies creates disorder in the atomic structure [1].

The influence of manganese dopant on YSZ structure and properties is interesting because during cell operation Mn ions can diffuse to electrolyte from cathode, which is often built of LaMnO₃ based material. Also, intentional mixing of electrodes and electrolyte material to create Mixed Ionic-Electronic Conductors (MIECs) is explored in order to reduce electrical losses during cell functioning [2-4].

The series of Mn_x(Y_{0,148}Zr_{0,852})_{1-x}O_{2-δ} ceramics [4] was systematically studied by means of X-ray absorption spectroscopy. EXAFS and XANES results show that the most significant changes in the measured spectra concern Mn ions and their environment, while the local structure evolution around Y and Zr is less pronounced. X-Ray diffraction and EXAFS measurements also indicate the presence of Mn₃O₄ precipitates for the samples with higher manganese content.

We show that gradual evolution of the local atomic environment around Mn ions in the YSZ phase takes

place upon increasing manganese content. This is due to changes in the average Mn oxidation state and structural relaxation caused by growing amount of oxygen vacancies.

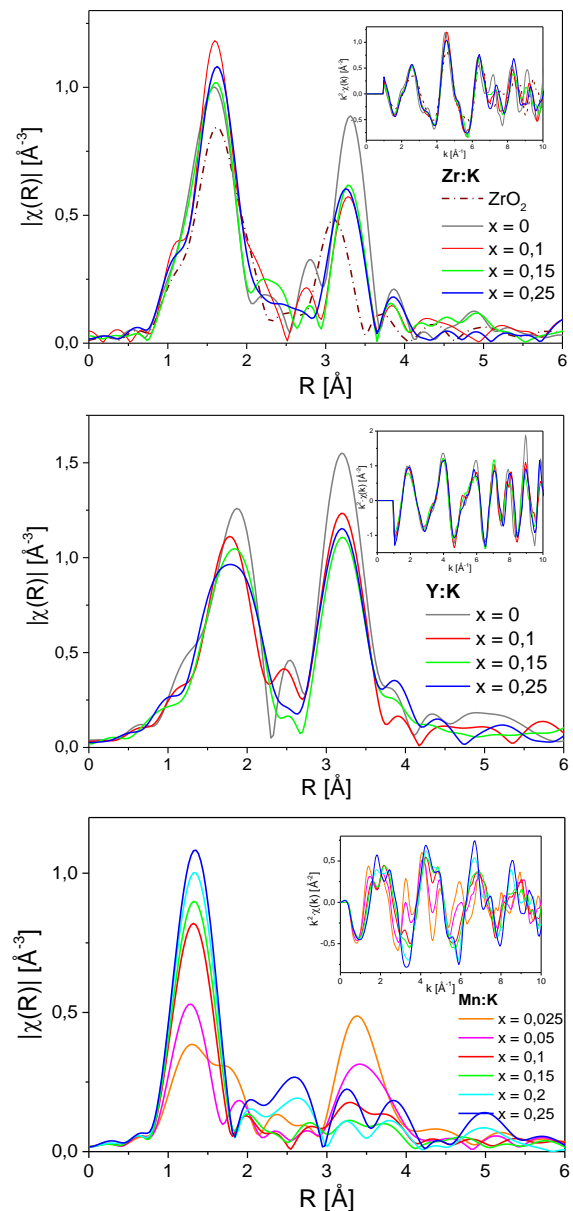


Figure 1. K edge EXAFS spectra in the R and k (inset) space of (top to bottom) Zr, Y and Mn.

- [1] E.H. Kisi and C.J. Howard, *Key Engineering Materials* **153-154** (1998) 1.
- [2] H. Chen, K. Cheng, F. Ye, W. Weng, *Ceramics International* **37** (2011) 1209.
- [3] J. H. Kim, G. M. Choi, *Solid State Ionics* **130** (2000) 157.
- [4] D. Pomykalska, M. M. Bućko, M. Rękas, *Solid State Ionics* **181** (2010) 48-52.