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Proton conductors of the type $Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ with tailored properties for application in electrochemical devices

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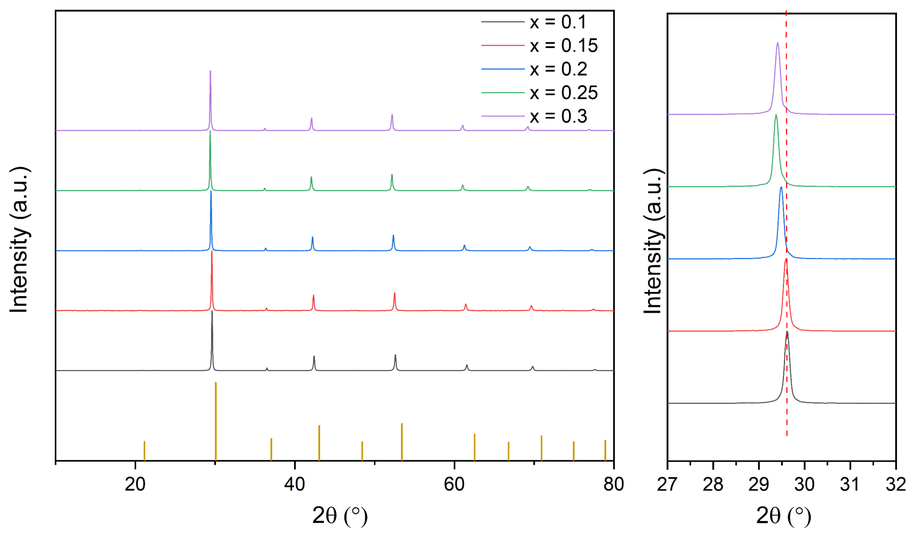
Abstract: The ever-increasing global energy demand has accelerated the consumption of fossil fuels, which causes a number of serious environmental problems. The solid oxide fuel and electrolysis cells (SOFC/SOEC) based on ceramic proton conductors converting chemical energy into electricity and vice versa with high efficiency at lower operating temperature, is one of the promising options to address the energy issue. The perovskite type crystals of doped $BaCeO_3$ and $BaZrO_3$ are nowadays the most frequently studied proton conductors. $BaCeO_3$ shows high protonic conductivity but low chemical stability in H2O and CO_2 atmosphere. On the contrary, $BaZrO_3$ has high chemical stability but low protonic transport ability at the grain boundary . Nevertheless, the balance of conductivity and chemical stability can be achieved by adjusting the ratio of Zr/Ce in the solid solution of Ba(Zr, Ce)O_3, and previous studies showed that the phase structure is stable under CO_2 and H_2O atmosphere when the content of Zr is higher than 50%. Moreover, acceptor (Y, Yb, Ho and Gd et al.) doping strategies are always employed to increase the amount of oxygen vacancies and thus increase the proton conductivity. A systematic investigation of material properties in the $Ba_{1.015}Zr_{0.8-x}Ce_{0.2}Y_xO_{3-\delta}$ (BZCY) series where x= 0.1 - 0.3 has been carried out to elucidate the effect of Zr-to-Y ratio at fixed Ce content and Ba over-stoichiometry of 1.5 mol%. Phase evolution, structural and microstructural features were correlated with the electrical properties of compounds in the series. Their chemical stability was tested under relevant operating conditions in the range of 700 °C. Based on this, conclusions of their applicability as cell components could be drawn.

Phase and Microstructure



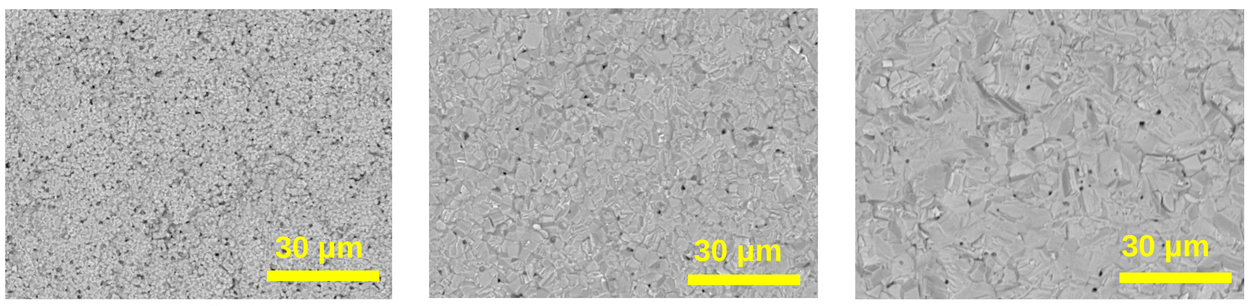
Phase structure:
Cubic perovskite

Cation radius:
Zr^{4+} : 0.080 nm
Ce^{4+} : 0.092 nm
Ce^{3+} : 0.103 nm
Y^{3+} : 0.090 nm

Figure 1 XRD patterns of the BZCY ceramics with different amount of Y

Table 1 Crystal parameters and relative density of BZCY ceramics with different amount of Y

Content of Y	x=0.1	x=0.15	x=0.2	x=0.25	x=0.3
Crystal parameters (Å)	4.2604	4.2656	4.2802	4.2959	4.2909
Relative density	92.3%	93.7%	95.5%	95.4%	96.2%



x = 0.1 x = 0.2 x = 0.3

Figure 2 SEM images of the fracture surface of BZCY cermaics with different amount of Y

Electrochemical Impedance Spectroscopy

- Three typical semicircles can be observed
- The conductivity of the sample with x value of 0.2 is higher than the one with x value of 0.1
- The conductivity of the sample with x value of 0.2 is 0.6 × 10^{-2} S•cm^{-1} at 600 °C

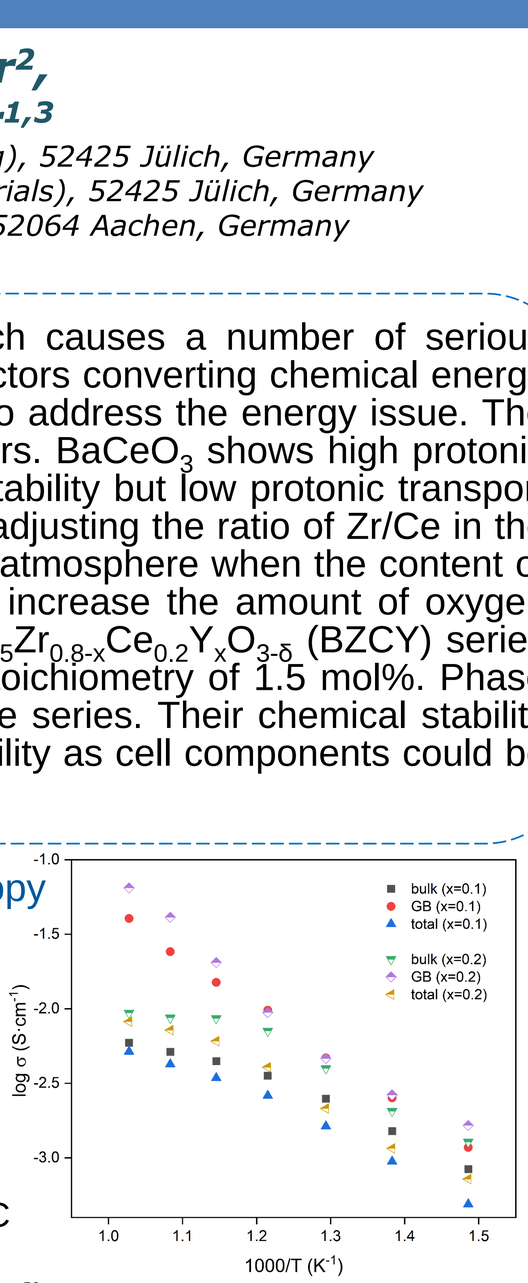
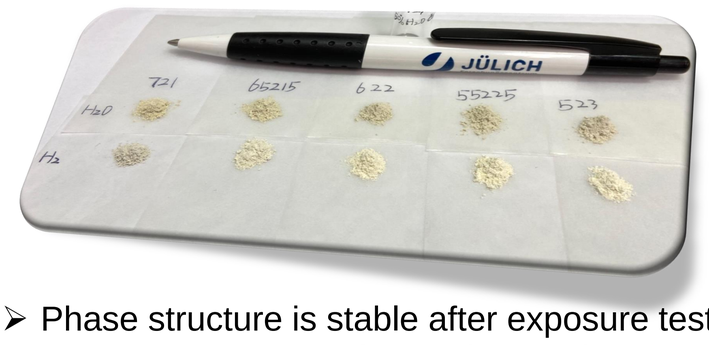


Figure 3 EIS and fitted conductivity of the samples with x value of 0.1 and 0.2 at elevated temperature

High temperature exposure experiments



- Phase structure is stable after exposure test
- Crystal parameters changed a lot after exposure test
- Apparently color change can be observed for the powders exposed to H_2/Ar

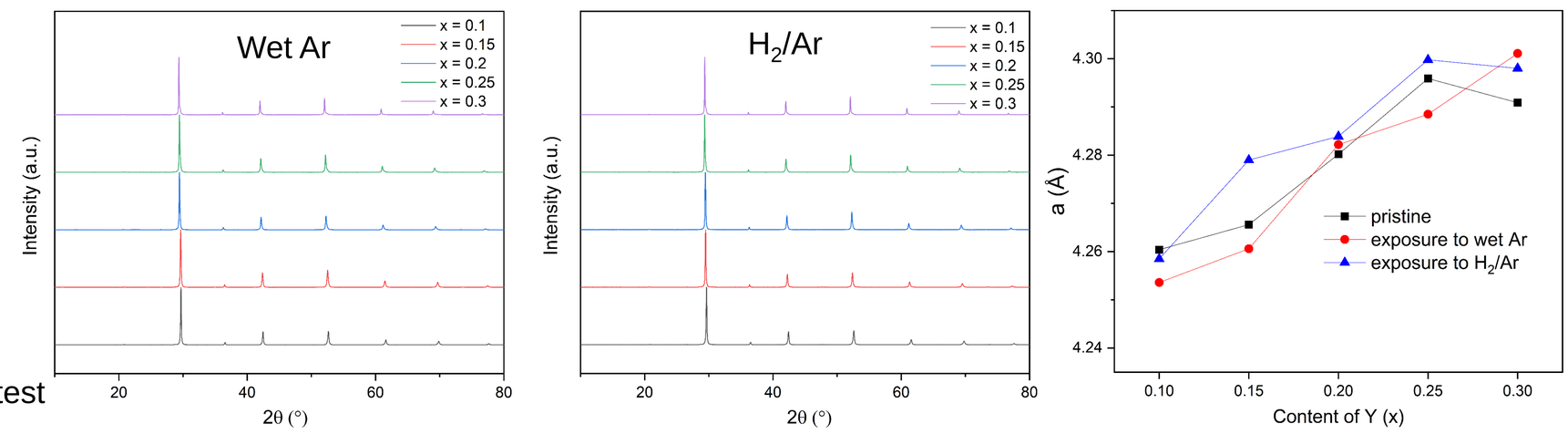


Figure 4 XRD patterns of the powders after exposure to wet Ar and H_2/Ar, and the crystal parameters comparison

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