Chemical Analysis of Elemental Excess and Depletion at Grain Boundaries of Ba(Ce,Zr,Y)$O_{3-\delta}$ Proton Conductors

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Proton conducting ceramics[1] play a key role in clean hydrogen-based electricity generation processes. Protonic ceramic fuel cells (PCFC) are promising due to reasons including lower operating temperature and absence of fuel dilution (allowing for high fuel utilization). A closed loop of fundamental theory, property measurement and structure characterization is essential in developing large-scale PCFC with improved efficiency along with these advantages. We focus on the system of Ba(Ce,Zr,Y)$O_{3-\delta}$ electrolyte materials owing to its very high bulk proton conductivity. Major problems of this system are the strongly blocking grain boundaries (GBs). In the present investigation, two sintering methods are applied: (i) Solid-state reactive sintering (SSRS) employing NiO which leads to the transient formation of a liquid phase[2], (ii) Spark-plasma sintering (SPS) of powders that are decorated with additives trying to decrease the excess positive change of the grain boundaries.

Here, we report on the elemental distribution and chemical variation in the vicinity of grain boundaries by quantitative energy-dispersive X-ray spectroscopy (EDX), electron energy-loss spectroscopy (EELS) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy. In a SSRS-sintered sample with GBs decorated by Ni, quantitative EDX at GBs showed excess of Ni, Y and deficiency of mainly Zr at the grain boundaries (Fig. 1). This confirms replacement of Zr by Y at the GB which partially compensates the grain boundary core charge and decreases the blocking character. In some samples GB excess of Ba was detected along with O deficiency indicating replacement of ABO_3 by BaO in the GB core.

We used EELS to analyze GBs in a SPS-sintered sample decorated with LaP$_3$O$_9$. In Figure 2 the existence of a minor amount of La is confirmed to be present in the region close to the boundary, but not inside the boundary core. Moreover, a change of the Ce valence state is observed from the decrease of Ce M_5 peak position[3]. More results and their correlation to factors influencing proton-conducting efficiency will be presented.
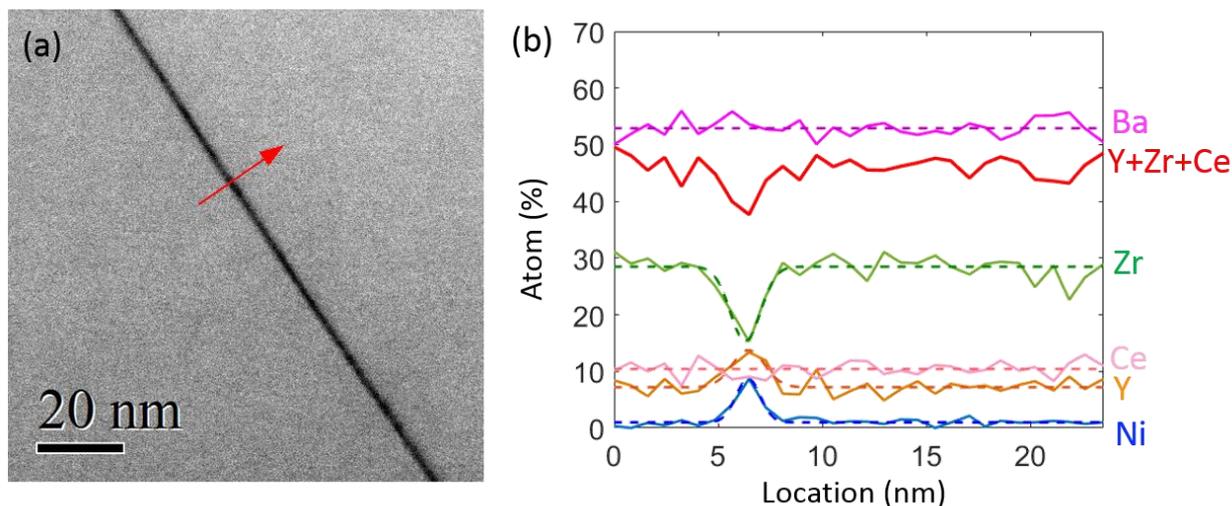
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Figure 1. (a) HAADF image of a SSRS_sintered Ni-doped $Ba_{1.015}Ce_{0.2}Zr_{0.664}Y_{0.136}O_{3-\delta}$ sample marking the analyzed grain boundary region by a red arrow; (b) EDX line profiles of all the elements (excluding O).
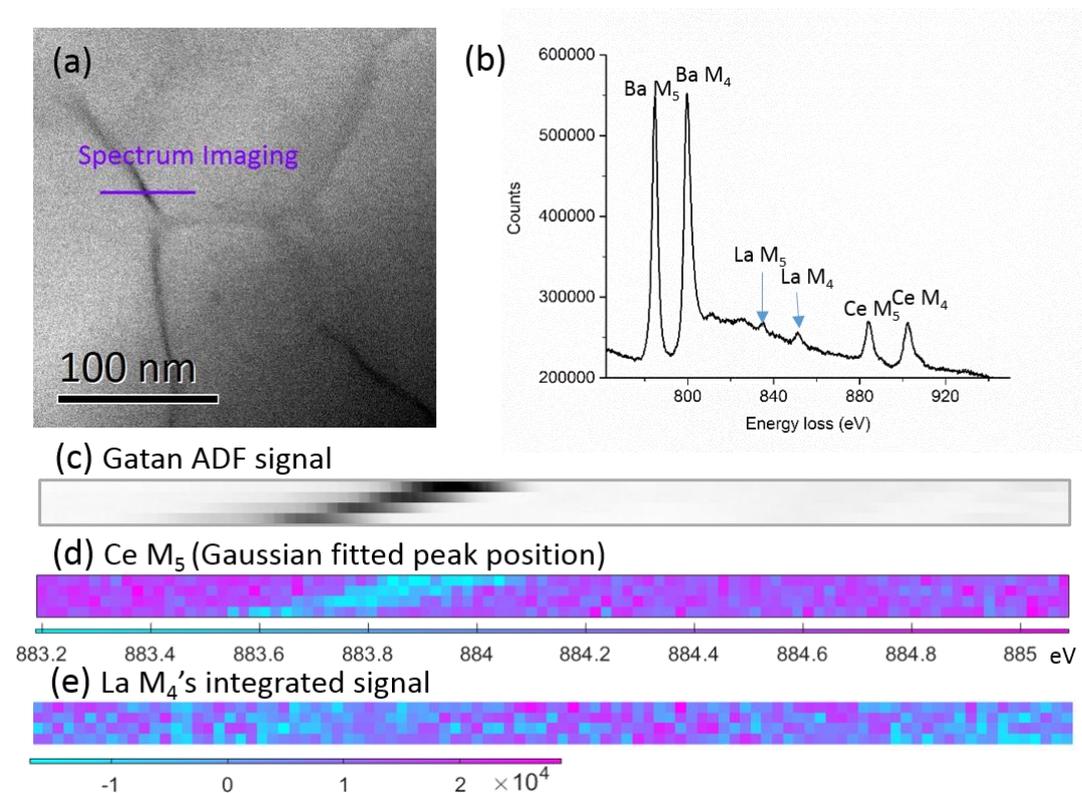
Figure 2. (a) HAADF image of a P-doped $Ba_{1.015}Ce_{0.2}Zr_{0.664}Y_{0.136}O_{3-\delta}$ sample marking the analyzed grain boundary region by a purple line; (b) A typical EELS spectrum integrated over 40 pixels of the EELS spectrum image; (c) ADF image, (d) Ce M_5 peak position and (e) La M_4 integrated signal extracted from the EELS spectrum image.