Direct observation of element distribution across ionic oxide grain boundaries using atomic-resolution STEM-EDS

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Grain boundaries (GBs) have a huge impact on the macroscopic properties of many materials in practical use. Owing to their local chemical inhomogeneity, GBs have exhibited novel functionalities which may not emerge in the bulk crystals. To understand and control GB properties for future material design, detailed knowledge on how the chemical inhomogeneity is induced at GBs is indispensable. Despite the fact that phenomenological description and theoretical prediction have been reported for ionic crystalline interface chemistry, the physical picture of GB chemistry is still under debate even in a simple ternary system of yttria-stabilized zirconia (YSZ), a popular electrolyte material in solid oxide fuel cells (SOFCs), due to a lack of direct experimental evidence. This is because it has been challenging to experimentally quantify the local chemistry especially for the light element of oxygen.

Here, we use atomic-resolution scanning transmission electron microscopy (STEM) energy-dispersive x-ray spectroscopy (EDS) to directly analyze the local GB chemistry in YSZ. Five types of YSZ bicrystals with different model GBs were first fabricated by diffusion bonding of two single crystals at 1600 °C for 15 h. STEM-EDS mappings were performed using JEOL JEM-ARM200CF, operated at an accelerating voltage of 200 kV. Our STEM-EDS system is equipped with double silicon drift detectors, which enables ultrahigh sensitivity X-ray detection.

Elemental mappings obtained by STEM-EDS provides direct chemical information in the vicinity of GBs. Our results show that Y atoms segregate to the GB, and the relative oxygen concentration in the GB is increased compared with the bulk. Combining with electron dynamical scattering theory, we confirmed that the increase of the GB oxygen concentration originates from the GB itself. These results strongly suggest that the equilibrium GB chemical distribution is dominated by the long-range electric interactions between charged GB cores and charged point defects. Furthermore, detailed atomic-resolution STEM EDS mapping analysis shows that Y atoms are not simply segregated in the GB homogeneously. Instead, they preferentially segregate to specific atomic sites in the GB. Figure 1 shows such an example with atomic resolution STEM EDS mappings in a coherent Σ3 [110]/(111) GB. We demonstrated that the structural factor of GB strain relaxation also affects the GB segregation for Y atoms, by combining with the atomic site-exchange Monte-Carlo simulations (Figure 1b). All the details will be discussed in the presentation.

References

[1] B. Feng, T. Yokoi, A. Kumamoto, M. Yoshiya, Y. Ikuhara and N. Shibata. Nat Comm (2016)
[2] B. Feng, N. Lugg, A. Kumamoto, Y. Ikuhara and N. Shibata. ACS Nano (2017)

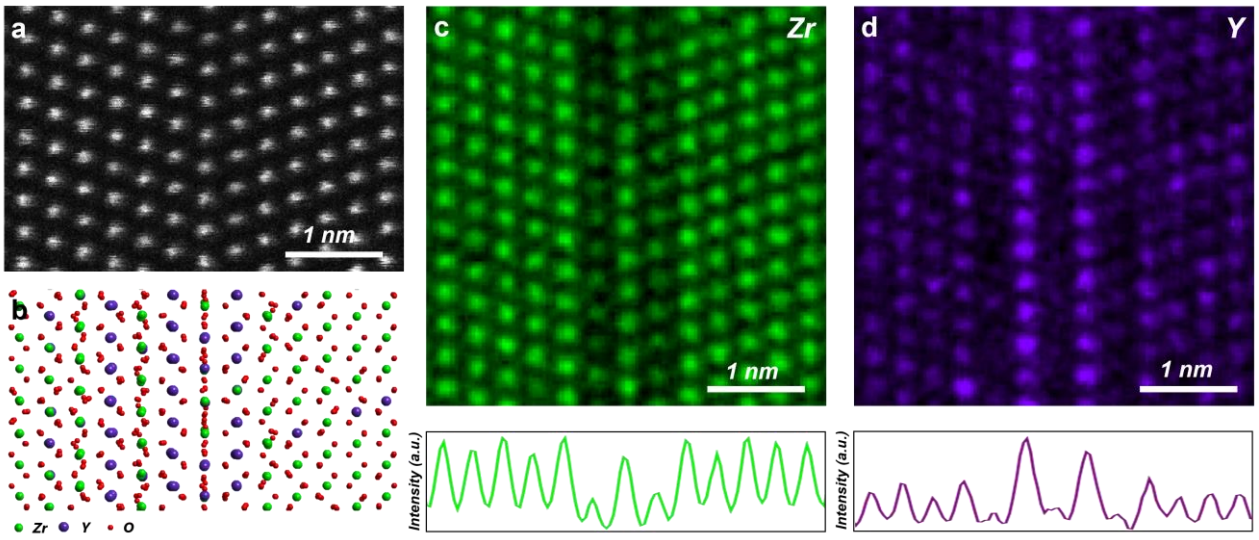

Figure 1. (a) HAADF-STEM image of the YSZ Σ3 [110]/(111) GB. (b) Theoretically predicted atomic structure at the GB. (c) and (d) STEM EDS maps and corresponding intensity profiles for Zr and Y, respectively.