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Two-dimensional Doping of Proton Conductors

Ionic conducting heterostructures are of interest to explore interfacial effects in solid state ionics and to foster their potential deployment in clean energy technologies such as solid oxide fuel cells. How to achieve ion conduction in heterostructures is therefore a fascinating and relevant question.

In this presentation, we will report on the first realization and study of a two-dimensionally doped ion conductor. This work is based on epitaxial BaZrO3–BaYOx heterostructures [1] in which entire ZrO2-layers of the BaZrO3 crystal are replaced by heterovalent layers (YOx). The resulting charge carriers reside in the immediate vicinity of the substituted layer. These heterostructures show – if hydrated - significant proton conductivities increasing with the number of interfaces. They are comparable, yet somewhat lower than those of hydrated Ba(Zr,Y)O3 ceramics. Pros and cons of 2d versus conventional 3d doping are discussed.

To explore the potential of inelastic electron tunneling spectroscopy to study ionic species at high-temperatures, we then use the same BaZrO3-based heterostructures as proton conductors and electron tunnel barriers in tunnel junction devices [2]. These junctions yield high-resolution inelastic tunneling spectra of protons diffused along the interfaces in BaZrO3–BaYOx-based tunnel barriers up to at least 400 K, breaking the previously established fundamental resolution limit by a factor of nine. By analyzing O–H bond vibrations, the existence of protons in the tunnel barriers is confirmed.

[1] P. Ngabonziza, R. Merkle, Y. Wang, P. A. van Aken, T. S. Bjørheim, J. Maier, and J. Mannhart, 2D Doping of Proton Conductors: BaZrO3-Based Heterostructures., Adv. Energy Mater. 11, 2003267 (2021).

[2] P. Ngabonziza, Y. Wang, P. A. van Aken, J. Maier, and J. Mannhart, Inelastic Electron Tunneling Spectroscopy at High-Temperatures., Adv. Mater. 33, 2007299 (2021).

Summary

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