High temperature and DC polarisation dependent ionic conduction in donor-doped lead zirconate titanate (PZT) investigated $^{18}$O tracer diffusion and impedance spectroscopy

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Donor doping significantly increases the amount of cation vacancies and suppresses oxygen vacancies in an oxide as demonstrated for perovskite-type materials such as BaTiO$_3$ and SrTiO$_3$. However, despite donor doping lead zirconate titanate (PZT), one of the most prominent ferroelectric materials, may exhibit a significant oxygen vacancy concentration. This can be attributed to the only partially controllable lead stoichiometry during preparation. Accordingly, many questions are still to be solved regarding partial conductivities of ions and electros.

In this contribution, we present results of a combined oxygen tracer diffusion and electrochemical impedance spectroscopy study on Nd-donor-doped PZT. Temperature and bias dependent measurements revealed information on the conduction mechanism and the defect distribution inside the material. At ca. 600°C a strong increase of ionic conductivity sets in, which leads to additional features in impedance spectra measured with ionically blocking electrodes and finally to thermally induced irreversible changes of the material. From the corresponding capacitance and resistance values oxygen vacancy concentrations and mobilities can be estimated. Complementary $^{18}$O tracer diffusion experiments, analysed by time-of-flight secondary ion mass spectrometry (TOF-SIMS) reveal many further details on ion transport properties: They show that on the one hand grain boundaries are responsible for the strongly enhanced ion transport above 600°C and on the other hand are the reason for the loss of ionic conduction over time. DC polarisation causes further changes in the sample which can again be monitored by $^{18}$O tracer diffusion. Under applied field, substantial changes of the grain boundary ion conduction are found already at much lower temperatures and with spatial variation; effects are most pronounced near to cathodes. Furthermore a significant time dependence of this bias induced grain boundary conduction is found upon increased polarisation times.