ADVANCED MATERIALS INTERFACES

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Supporting Information

Electrostatic Boundary Conditions and (Electro)chemical Interface Stability

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Interface Stability

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DIELECTRIC PROPERTIES OF STUDIED SAMPLES

Polarization hysteresis loops of the undoped and the La-doped PZST samples are shown in Fig. S1. The two samples exhibit a ferroelectric and an antiferroelectric hysteresis behaviour below the Curie temperature of about 200 °C, respectively. Identical polarisation hysteresis loops are measured with thin ITO electrode inside the vacuum system, indicating a homogeneous coverage and sufficient conductivity of the ITO electrode. The Curie temperature can be identified from the temperature dependent permittivity measurements, which are included in Fig. S1.
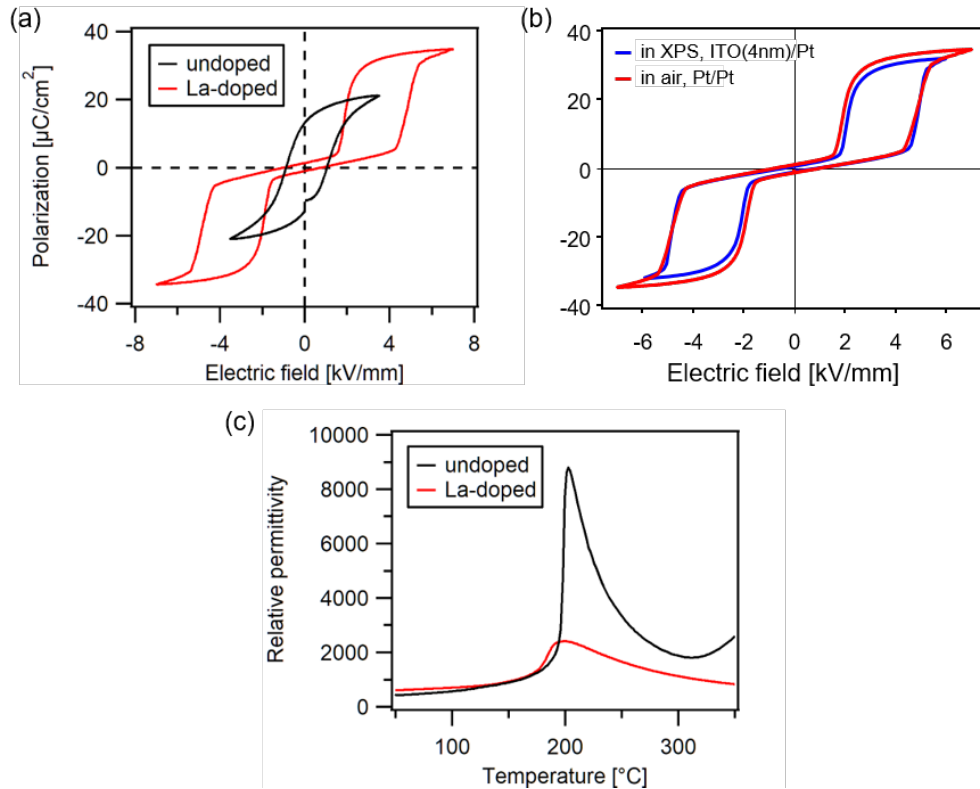
FIG. S1. (a) Polarisation hysteresis of the undoped and the 2 % La-doped PZST samples measured at room temperature in air with thick Pt electrodes at a frequency of 1 Hz; (b) comparison of polarisation hysteresis of La-doped PZST measured in air with thick Pt electrodes and in vacuum with a thick Pt bottom and a thin ITO top electrode; (c) temperature-dependent permittivity measured at 1 kHz.

CURRENTS AND CONDUCTIVITIES

Electrical currents through the samples were continuously recorded during X-ray photo-electron spectroscopy (XPS) measurements at $250\,^{\circ}$C with cathodic polarisation of the ITO electrode. The recorded currents are shown on left side in Fig. S2). Calculated 2-point conductivities are displayed on the right. It is observed that the electrical conductivity of the undoped PZST sample increases with electric field up to a value of $\sim 10^{-6}\,$S/cm. In contrast, the conductivity of the La-doped PLZST sample, which is more than 3 orders of magnitude lower than that of the undoped one, initially remains constant and even decreases for higher fields. Please also note that substantially higher electric fields have been applied to the PLZST sample. The different field dependencies are likely related to different concentrations of oxygen vacancies, which are expected to be higher for the nominally undoped PZST [1, 2]. For an electric field of $20\,$V/mm, the conductivity of the undoped sample increases with time. This is the typical resistance degradation behaviour [3, 4]. For higher fields, the conductivity does not show an increase with time but still increases with applied field. In contrast to PZST, the conductivity of donor-doped PLZST remains constant for low fields. There is no indication for degradation. The conductivity even decreases for higher electric fields. Within the range of electric fields applied in this work, no diverging electrical currents are observed, indicating stable operation of the electrochemical cells throughout the complete experiments for both samples.

The higher conductivity of the undoped sample corresponds well with literature reports on the electrical conductivity of Pb-based perovskites, which indicate p-type conduction of nominally undoped samples [1, 5]. By intentional donor doping, the p-type conduction is suppressed and a much lower n-type conductivity is established. For Ti-rich $Pb(Zr,Ti)O_3$ compositions, p-type conduction has been associated with holes trapped on Pb^{2+}-sites, while n-type conduction of donor-doped materials has been associated with electron trapping on Ti^{4+}-sites [4].
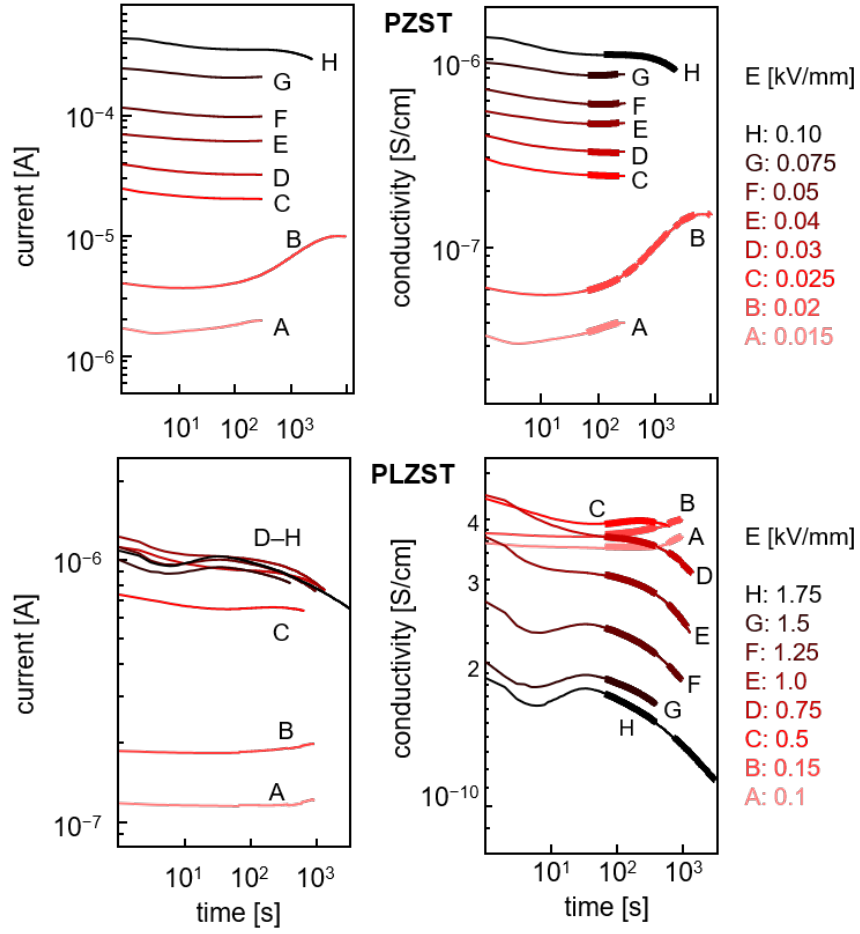
FIG. S2. Currents (left) and calculated conductivity (right) for undoped (top) and La-doped PZST (bottom) during stepwise increase of applied electric field. The times at which XP spectra are recorded are indicated by thick lines.

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