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ABSTRACT:

Proton Activated Gigantic Increase of Electronic Conductivity in Monolithic $SrTiO_3$ Single Crystals

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Single crystals of undoped strontium titanate (STO) exhibit a very low electrical conductivity at room temperature on the order of nS/cm. Electronic and oxygen vacancy mediated electrical conductivity is reaching the mS/cm range only at considerably elevated temperatures of 800°c and above. (Balachandran and Eror 1981). As a continuation of work presented at a previous DSL conference we describe and rationalize the activation of electrical conductivity in STO at modestly elevated temperature below 200°C.

To this end single crystals of STO have been coated with thin (100nm) Pt electrodes on both sides. Subsequently these samples are exposed to an electric field of typically 100 V/cm at 180°C in hydrogen atmosphere (200mbar). Within several hours the conductivity increases by more than 5 orders of magnitude reaching close to the mS/cm regime.

Extensive studies demonstrate that the activation is unambiguously due to proton transport through the volume of the sample. The macroscopical conductivity, however, is clearly not due to protons but to electrons. This mechanism is supported by experiments with varying thickness of the samples at different electric fields, further comparing hydrogen and deuterium atmospheres. Nernst-Planck-Poisson calculations confirm that the time evolution of currents measured follows the transport of protons (deuterons) through the bulk of the sample. The increase in conductivity is accompanied by a visible colour change of the crystals from colourless to yellow.

We propose a model of "field-induced chemical doping" to explain this transformation. Hydrogen is converted to protons at the Pt/STO interface in the presence of the electric field. Protons are driven through the bulk of the sample in the electric field. This effectively leads to a doping of the sample which in turn leads to electronic conductivity with an activation energy of 0.3 eV.

The resulting activated STO crystals exhibits excellent hydrogen sensing properties at room temperature, detecting molecular hydrogen (H2) over an exceptionally wide partial pressure range from 0.00001 mbar to 500 mbar with an accuracy of a few percent.

References

Balachandran, U.; Eror, N.G., (1981): Electrical conductivity in strontium titanate1981. In: Journal of Solid State Chemistry 39 (3), p. 351–359.