

DEFECT CHEMISTRY AND OXYGEN ION CONDUCTION IN DONOR- DOPED LEAD ZIRCONATE TITANATE (PZT)

C. Slouka, G. Holzlechner, L. Andrejs, J. Fleig

Vienna University of Technology, Institute of Chemical Technologies and Analytics,
Getreidemarkt 9, 1060 Vienna, Austria; e-mail: christoph.slouka@chello.at

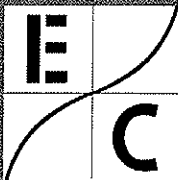
Ionic and electronic defects strongly affect many properties of electroceramic materials. A powerful tool to effectively influence these materials properties is doping. Donor doping generally decreases significantly the amount of oxygen vacancies within a material. However, despite donor doping, lead zirconate titanate (PZT), one of the most prominent ferroelectric materials used in multiple technological devices such as generators, motors, ultrasonic transducers, actuators or non-volatile memories, may exhibit a significant oxygen vacancy concentration. This can be attributed to the only partially controllable loss of lead oxide during preparation. Accordingly, many questions are still to be solved regarding oxygen chemical diffusion and partial conductivities of ions and electrons in PZT.

In this contribution, we present results of an impedance spectroscopic study and oxygen tracer diffusion experiments, monitored by TOF-SIMS on Nd-doped PZT. Temperature and oxygen partial pressure were varied and corresponding time-dependent and steady state measurements allowed conclusions on the nature of the conducting charge carriers (electrons, holes, oxygen vacancies) and the chemical diffusion coefficients. Furthermore oxygen tracer experiments, especially at high temperatures (> 600 °C), allow determining bulk and grain boundary oxygen diffusion coefficients.

It will also be shown that substantial oxide ion conduction sets in at temperatures above 600 °C and leads to additional features in impedance spectra measured with ionically blocking electrodes and finally to thermally induced irreversible changes of the material. These changes are interpreted in terms of lead oxide evaporation and, hence, significant changes in the defect chemical situation leading to annihilation of oxygen vacancies along grain boundaries. Therefore, a time dependent decrease of ion conduction is observed in impedance spectroscopy and tracer diffusion experiments. From the corresponding capacitance and resistance values oxygen vacancy concentrations and mobilities can be estimated and compared to results of complementary DC experiments.

Defect Chemistry and Oxygen Ion Conduction in Donor-Doped Lead Zirconate Titanate (PZT)

Christoph Slouka, Gerald Holzlechner, Lukas Andrejs, Jürgen Fleig

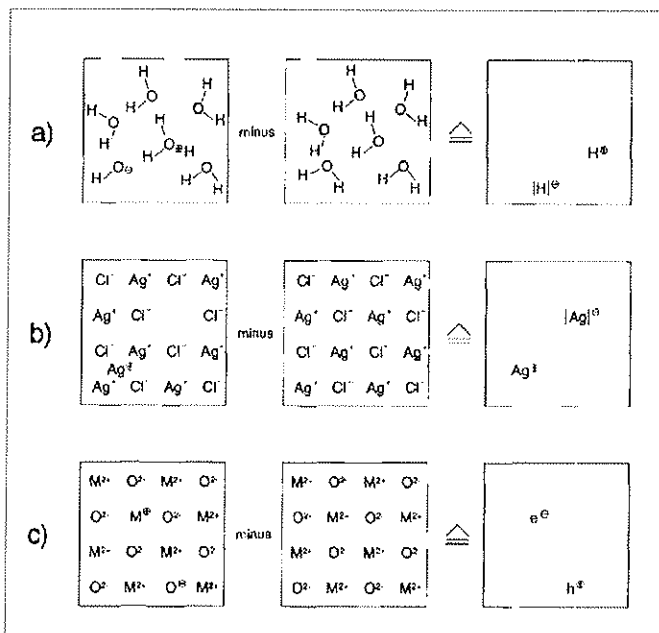


Intrinsic defects in three different media:

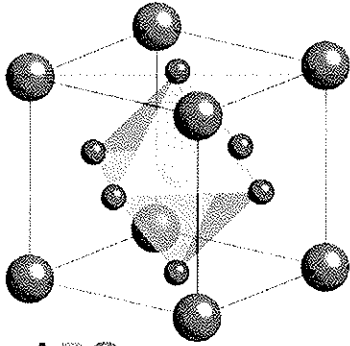
- Disorder in water at pH = 7
- Solid AgCl with interstitial Ag⁺ ions
- e-h formation in oxides

Realization of defects in solids:

- Intrinsic ionic disorder** - thermally activated process
- Extrinsic defects** - doping of materials
- Nonstoichiometry** - oxidation processes in the lattice
- Intrinsic electronic disorder**



Maier, J.: Physical Chemistry of Ionic Materials. 2005



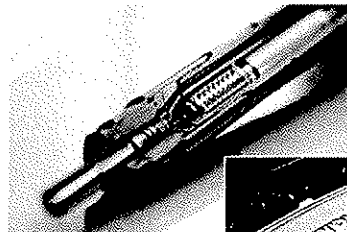
PZT – solid solution of lead titanate and lead zirconate near the morphotropic phase boundary (no phase separation)

Perovskite structure below T_c (Curie temperature): piezo- and ferroelectric

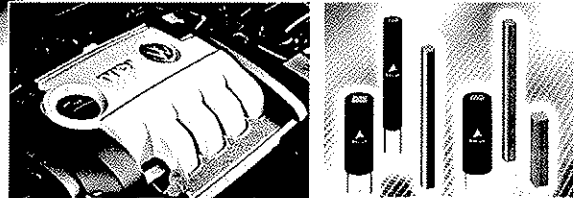
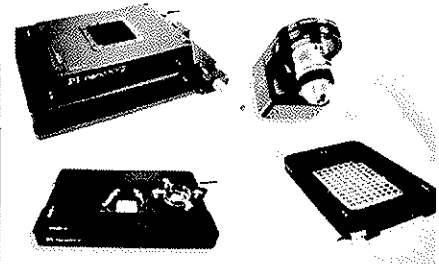
Point defects play a major role in the performance parameters of ferroelectrics:

- donor doping – higher valence than replaced $\rightarrow V''_{Pb}$ (**soft PZT**)
- acceptor doping – lower valence than replaced $\rightarrow V''_{O}$ (**hard PZT**)

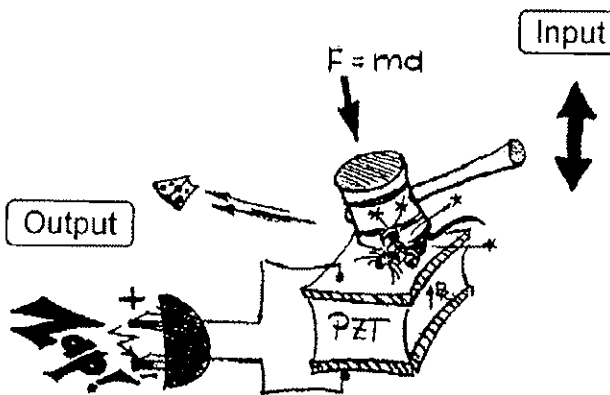
Injection devices



micromanipulators



GENERATOR

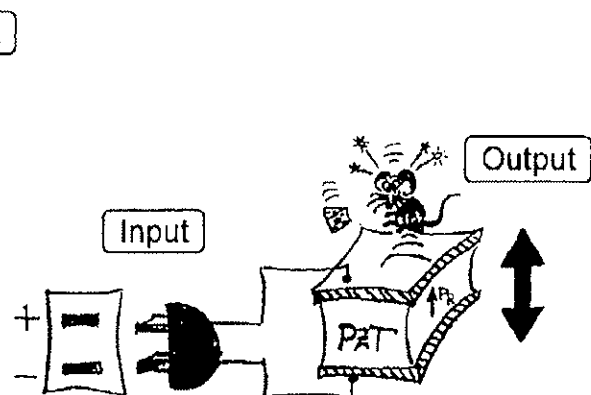


Direct Effect

- Direct piezo-effect

$$D = d E + \epsilon^T E : \text{generator}$$

MOTOR



Converse Effect

- Reverse piezo-effect

$$s = s^E T + d E : \text{motor}$$

- PZT: good knowledge about processing available
- nevertheless defect chemistry is less understood than in other perovskites such as BTO and STO, due to the **uncontrollable loss of PbO** during sintering
- **Defect chemistry often unknown !!**

Hole or electron conduction ?

How much oxygen vacancies ?

• Identification through **Brouwer diagrams** (pO_2 vs. concentration)

• concentration ~ conductivity ($\sigma = z \cdot e \cdot n \cdot u$) available through EIS

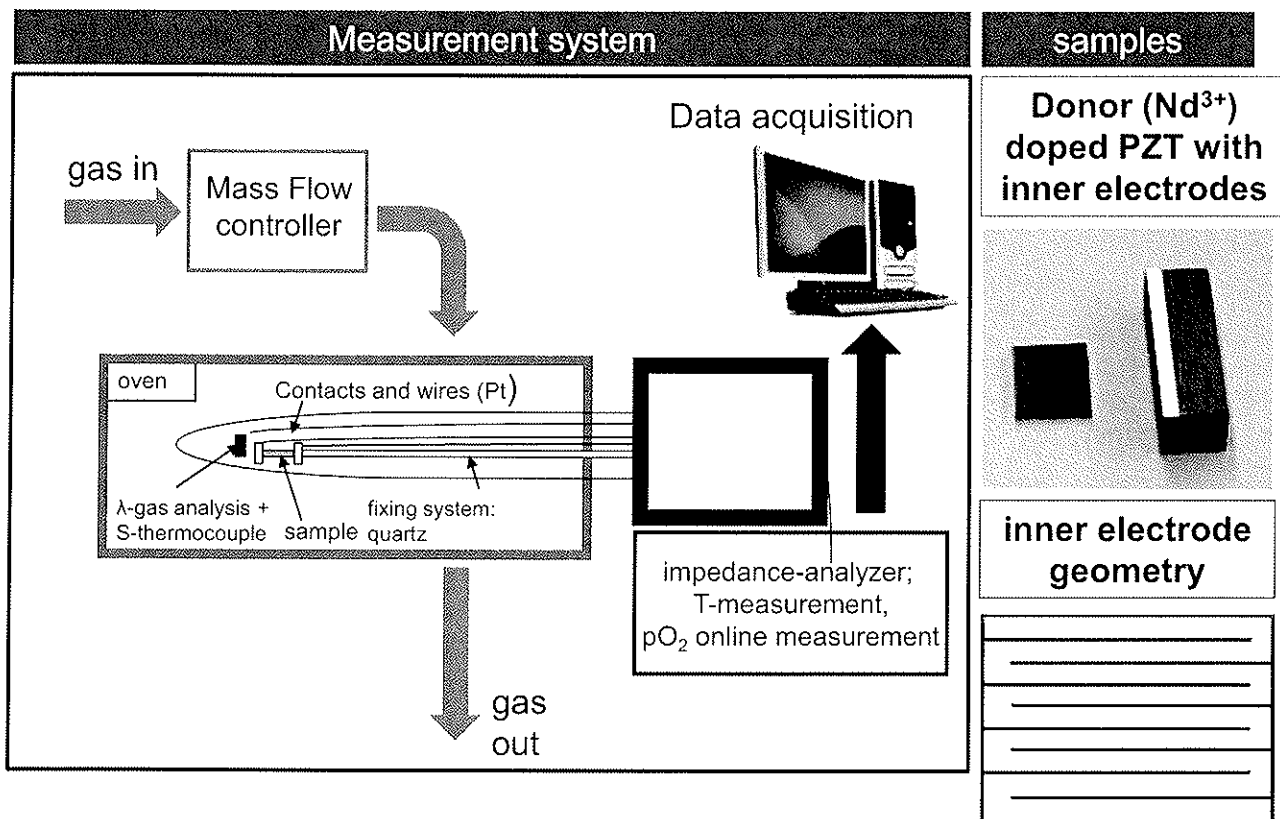
• Identification through **EIS (second semicircle)**

• **^{18}O -tracer:** diffusion coefficients for ^{18}O measured with ToF-SIMS

1/28/2014

Methods : Impedance Spectroscopy / ^{18}O – tracer exchange

5



1/28/2014

6



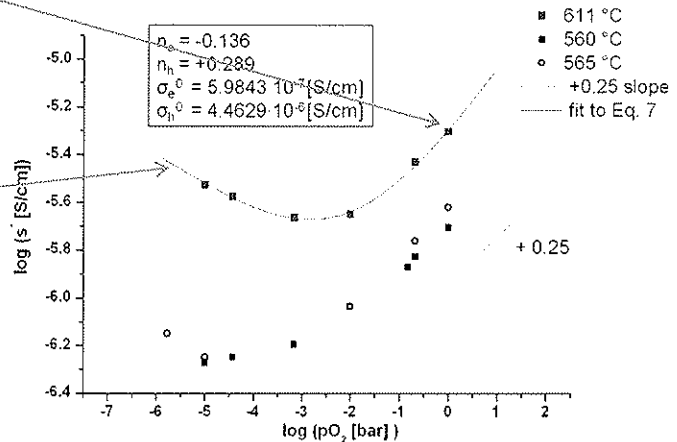
$$\frac{[h^{\bullet}]^2}{[V_{O}^{\bullet\bullet}]} = K_P P_{O_2}^{1/2}$$

$$[h^{\bullet}] = K_P^{-1/2} P_{O_2}^{1/4} [V_{O}^{\bullet\bullet}]^{1/2}$$

$$nil = e' + h^{\bullet}$$

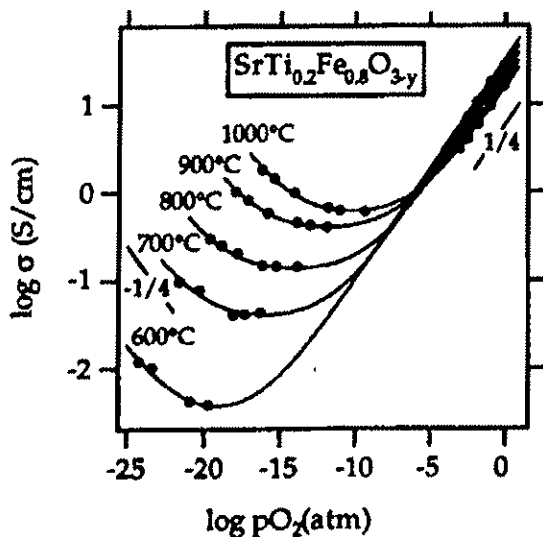
$$[e'] = K_c K_P^{-1/2} P_{O_2}^{-1/4} [V_{O}^{\bullet\bullet}]^{-1/2}$$

- In general donor doping leads to **e⁻ and cation vacancies** → suppression of $V_{O}^{\bullet\bullet}$ and h^{\bullet}
- Obvious transition from hole (+1/4) to electron (-1/4) conduction visible in PZT

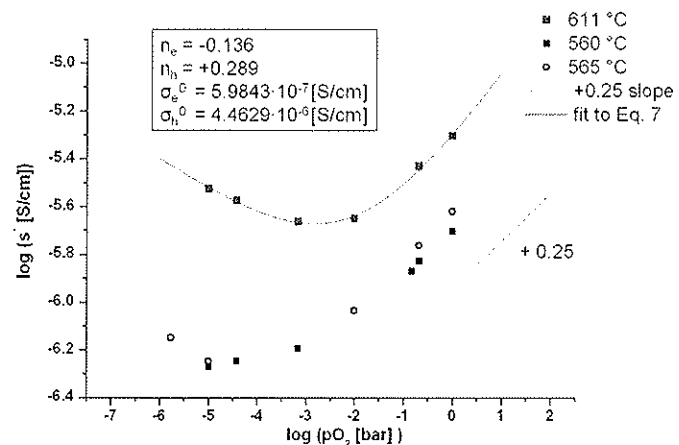


1/28/2014

7



S. Steinsvik, R. Bugge, J. O. N. Gjønnes, J. Taftö and T. Norby, *Journal of Physics and Chemistry of Solids* 58 (6), 969-976 (1997).

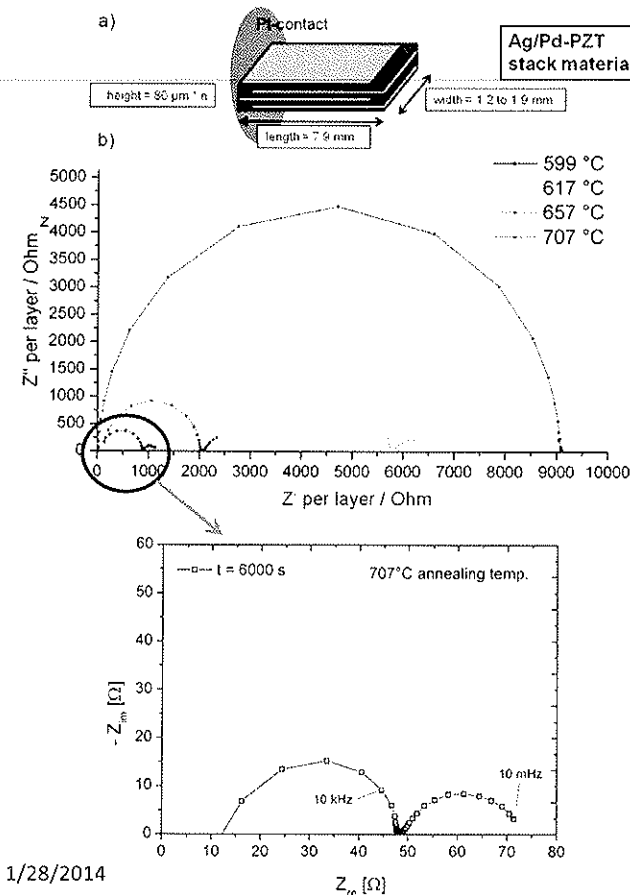


- Despite donor doping → hole conducting regime!
- Evaporation of PbO during processing → **effective acceptor doping**
- Movement of Ag^+ into PZT (electrodes) enhances the effect

$$[A'_{eff}] = 2 [V''_{Pb}] - [D^{\bullet}] + [Ag'_{Pb}]$$

1/28/2014

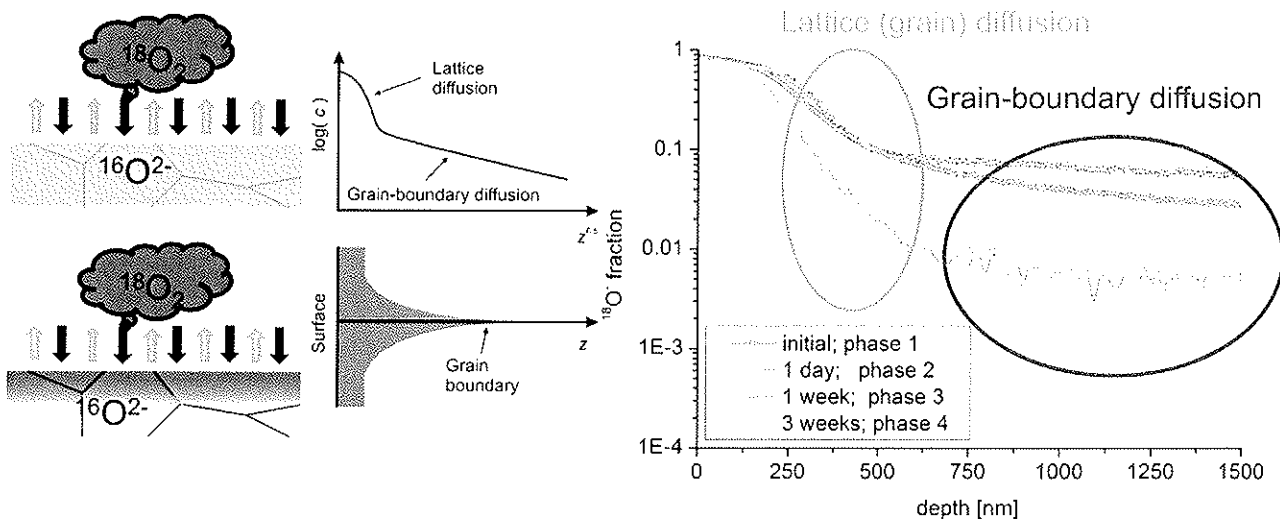
8



- Spectra characteristic changes drastically with T and time. Interpretation as ionic conductivity (oxygen vacancies) decreases with time
- Most possible reason is PbO evaporation or cation movement at elevated temperatures decreasing oxygen vacancy concentration
- Oxygen vacancy concentration calculated (not shown) to be about 2 ppm
- With Nernst-Einstein equation approximately $D_V = 2.36 \cdot 10^{-6}$ cm/s
- **Open question: where is the ionic conductivity located: grain or grain boundary ?**

1/28/2014

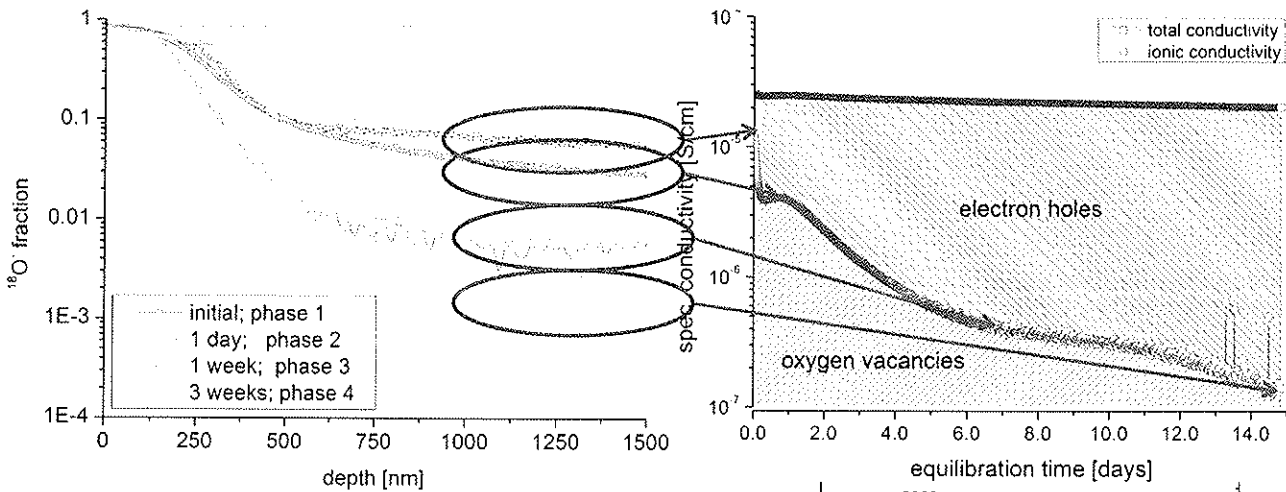
9



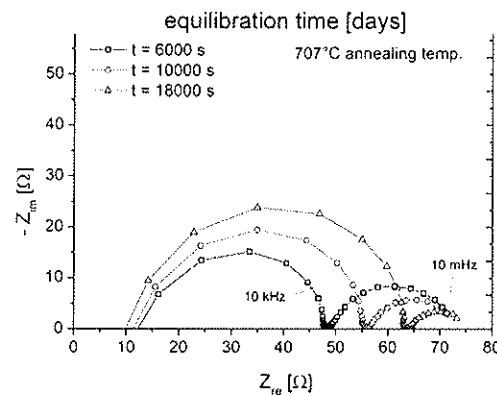
- Tracer profiles: reduction of tracer incorporation in the grain boundaries even after one day
- after 3 weeks tracer concentration is on the natural abundance of ¹⁸O in the grain boundaries.
- Yet unknown artifacts in the grain region after 3 weeks: to an enhanced incorporation of ¹⁸O

1/28/2014

10



- Loss visible in EIS is visible in the grain boundary part of ^{18}O -tracer experiments!
- **Less of ionic conductivity can be attributed to the grain boundary region in PZT!**



1/28/2014

11

- The partial pressure dependence is shown (Brouwer diagram) revealing an **shift from hole to electron** conduction.
- Nominally donor doped PZT becomes effectively **acceptor doped** during preparation, caused by PbO evaporation during sintering
- One semicircle is visible in EIS up to approx. 650 °C Above the change in the spectra is caused by **significant ionic conduction** blocked at electrodes.
- Ionic conduction was identified to be **situated at the grain boundaries** of the PZT ceramics by ^{18}O -tracer exchange and ToF-SIMS analysis. Ionic conduction vanishes in time

1/28/2014

12



Thanks to the



Christian Doppler
Forschungsgesellschaft

for funding!

Thanks to the whole group of Electrochemistry at TU Wien

