Defect structure and oxygen diffusion in PZT ceramics

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Introduction

Ferroelectrics are of great technical interest because of their sensing and actuator properties e.g.:

• „smart materials“ (e.g. change of damping behavior)
• thin films for non-volatile memory applications

However, the materials suffer from fatigue!
(mechanically and electrically)

electrical fatigue under polarization reversal is attributed to the hindrance of domain wall mobility with point defects and electrochemical degradation

The exact fatigue mechanisms are still poorly understood

Consequently, the investigation of point defects and their diffusion are of great interest
Positron Annihilation Spectroscopy

\[ \beta^+ \text{-decay} \]
\[ ^{22}\text{Na} \rightarrow ^{22}\text{Ne} \]

1275 keV
Birth-\( \gamma \)

\( \text{Start} \)

\( \text{PM} \)

\( \text{TAC} \)

\( \text{MCA} \)

Log N

2 Annihilation-\( \gamma \)'s
511 keV

\( \text{Stop} \)

PM

Diffusion

typical diffusion length
\( \sim \lambda \ 0.1 \ \mu\text{m} \)

Typical diffusion length

\( \sim \lambda \ 0.1 \ \mu\text{m} \)

Trapping
@ defect

\( \text{PM} \)

Differentiation

Typical diffusion length

\( \sim \lambda \ 0.1 \ \mu\text{m} \)
Trapping model

e. g. for a single defect
rate eq.:

\[
\frac{d n_b}{dt} = -\lambda_b n_b - \kappa_d n_b
\]

\[
\frac{d n_d}{dt} = -\lambda_d n_d + \kappa_d n_b
\]

\[
D(t) = I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right)
\]

\[
\kappa_d = \mu C = I_2 \left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right) = \frac{I_2}{I_1} \left(\frac{1}{\tau_b} - \frac{1}{\tau_d}\right)
\]

\[
\tau_2 = \frac{1}{\lambda_d} ; \quad \tau_1 = \frac{1}{\lambda_b + \kappa_d}
\]
The lifetime spectrum is given by:

\[ N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \cdot \exp \left\{ -\frac{t}{\tau_i} \right\} \]

\( k \) defects yield to \( k+1 \) Lifetime-components \( \tau_{k+1} \)!
### Ionic Radii

<table>
<thead>
<tr>
<th></th>
<th>Pauling [pm]</th>
<th>4-coordinate [pm]</th>
<th>6-coordinate [pm]</th>
<th>8-coordinate [pm]</th>
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<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>120</td>
<td>-</td>
<td>133</td>
<td>143</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>115</td>
<td>-</td>
<td>117.2</td>
<td>130</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>80</td>
<td>73</td>
<td>86</td>
<td>98</td>
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<tr>
<td>Ti$^{4+}$</td>
<td>68</td>
<td>56</td>
<td>74.5</td>
<td>88</td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>70</td>
<td>62</td>
<td>-</td>
<td>88</td>
</tr>
</tbody>
</table>

[1] www.webelements.com
Effect of La\(^{+3}\) and Nb\(^{+5}\) -doping

**Pb\(^{+2}\)-site**
- Ionic radii:
  - \(r(\text{La}^{+3})/r(\text{Pb}^{+2}) \approx 0.88\)
  - \(r(\text{Nb}^{+5})/r(\text{Pb}^{+2}) \approx 0.62\)
- The dopant induces \(V_{\text{Pb}}\)

**Zr\(^{+4}/\text{Ti}^{+4}\)-site**
- Ionic radii:
  - \(r(\text{Nb}^{+5})/r(\text{[Zr}_{60}\text{Ti}_{40}]^{+4}) \approx 0.94\)
    - The dopant induces \(V_{\text{Pb}}\)
  - \(r(\text{La}^{+3})/ r(\text{[Zr}_{60}\text{Ti}_{40}]^{+4}) \approx 1.38\)
    - Dopant induces \(V_{\text{O}}\)

\(a_0 : 4.102 \text{ Å}\)
\(\alpha, \beta, \gamma : 89.68^\circ\)
The lattice parameter $a_0$ as well as the cell volume monotonically decreases for both La$^{+3}$ and Nb$^{+5}$ doping.

According to the ionic radii this suggests that La$^{+3}$ occupies Pb-sites and Nb$^{+5}$ Zr/Ti-sites exclusively.
Cell volume

doped Pb(Zr$_{0.6}$Ti$_{0.4}$)O$_3$

La

Nb
Defect Chemistry

La\(^{3+}\) on Pb\(^{2+}\) site
\(\Rightarrow 2 \text{La}_A \Rightarrow V_{\text{Pb}}\)

Nb\(^{5+}\) on Zr/Ti\(^{4+}\) site
\(\Rightarrow 2 \text{Nb}_B \Rightarrow V_{\text{Pb}}\)
Calculated Positron Lifetimes

DFT-pseudopotential, atomic superposition methods

<table>
<thead>
<tr>
<th>Material</th>
<th>PbTiO$_3^*$</th>
<th>LaCoO$_3^*$</th>
<th>BaTiO$_3^*$</th>
<th>PZT(60/40)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau$ [ps]</td>
<td>$\tau$ [ps]</td>
<td>$\tau$ [ps]</td>
<td>$\tau$ [ps]</td>
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<tr>
<td>bulk</td>
<td>147</td>
<td>129</td>
<td>152</td>
<td>168</td>
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<tr>
<td>$V_A$</td>
<td>280</td>
<td>275</td>
<td>293</td>
<td>270</td>
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<tr>
<td>$V_B$</td>
<td>175</td>
<td>173</td>
<td>204</td>
<td>195</td>
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<tr>
<td>$V_O$</td>
<td>152</td>
<td>145</td>
<td>162</td>
<td>163</td>
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<td>2$V_O$</td>
<td>160</td>
<td></td>
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<tr>
<td>$V_A$,$V_O$</td>
<td>284</td>
<td>280</td>
<td></td>
<td>305</td>
</tr>
</tbody>
</table>


This work with W. Puff and G. Bischoff, TU Graz

A. G. Balogh
Varying Zr/Ti ratio

![Graph showing varying Zr/Ti ratio](image)

- **x Pb(Zr$_x$Ti$_{1-x}$)O$_3$**
- Lifetimes $\tau_1$ and $\tau_2$
- Intensity $I_2$ [%]

Transition regions:
- Tetragonal
- Morphotropic
- Rhombohedral

Zr/Ti ratio: 0.35, 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, 0.70, 0.75
Lifetime data of donor doped samples

- **Donor doping** yields to the saturation of lifetime component $\tau_2 \sim 300\text{ps}$ ($V_{\text{Pb}}$)
- $\tau_2$ 255-305 ps
- As $\tau_2$ saturates, $\tau_{\text{bulk}}$ disappears, sat. $\tau_1$ can be attributed to $V_0 \tau \sim 170\text{ps}$
XPS Pb 4f

XPS
Mg Kα

BE [eV]
N(E) [a.u.]

Pb 4f
5/2
7/2
4.9 eV
1.5 eV
4.8 eV

6% La
1% La
undoped

XPS
Al Kα

BE [eV]
N(E) [a.u.]

Pb 4f
5/2
7/2
1.5 eV

6% La
2 keV Ar⁺
O-plasma
About the defect structure of PZT - compensation mechanisms

(i) Vacancy formation (e.g. for La$^{3+}$-, Nb$^{5+}$-doping):

La$^{3+}$ on the A-site:

\[3 \text{Pb(Zr/Ti)}O_3 + \text{La}_2\text{O}_3 \rightarrow 3(\text{La}^\bullet_{\text{Pb}})_{2/3} (\text{V}^\text{''}_{\text{Pb}})_{1/3} (\text{Zr} / \text{Ti})O_3 + 3 \text{PbO}\]

\[3 \text{Pb(Zr/Ti)}O_3 + 2 \text{La}_2\text{O}_3 \rightarrow 4 \text{La}^\bullet_{\text{Pb}} (\text{V}^\text{'''}_{(\text{Zr/Ti})})_{1/4} (\text{Zr} / \text{Ti})_{3/4} O_3 + 3 \text{PbO}\]

La$^{3+}$ on the B-site:

\[2 \text{Pb(Zr/Ti)}O_3 + \text{La}_2\text{O}_3 \rightarrow 2 \text{Pb La}^\prime_{(\text{Zr/Ti})} (\text{V}^\text{''}_{O})_{1/2} O_{5/2} + 2 (\text{Zr} / \text{Ti})O_2\]

Nb$^{5+}$ on the B-site:

\[\text{Pb(Zr/Ti)}O_3 + \text{Nb}_2\text{O}_5 \rightarrow 2 \text{Pb}^{1/2} (\text{V}^\text{''}_{\text{Pb}})_{1/2} \text{Nb}^\bullet_{(\text{Zr/Ti})} O_3 + (\text{Zr} / \text{Ti})O_2\]

\[5 \text{Pb(Zr/Ti)}O_3 + 2 \text{Nb}_2\text{O}_5 \rightarrow 5 \text{Pb} (\text{Nb}^\bullet_{(\text{Zr/Ti})})_{4/5} (\text{V}^\text{'''}_{(\text{Zr/Ti})})_{1/5} O_3 + 5 (\text{Zr} / \text{Ti})O_2\]

Nb$^{5+}$ on the A-site:

\[5 \text{Pb(Zr/Ti)}O_3 + \text{Nb}_2\text{O}_5 \rightarrow 5 (\text{Nb}^\bullet_{\text{Pb}})_{2/5} (\text{V}^\text{''}_{\text{Pb}})_{3/5} (\text{Zr} / \text{Ti})O_3 + 5 \text{PbO}\]

\[\text{Pb(Zr/Ti)}O_3 + 2 \text{Nb}_2\text{O}_5 \rightarrow 4 \text{Nb}^\bullet_{\text{Pb}} (\text{V}^\text{'''}_{(\text{Zr/Ti})})_{3/4} (\text{Zr} / \text{Ti})_{1/4} O_3 + \text{PbO}\]
(ii) Conduction states

allow a fraction of free e\(^-\) or h\(^+\) in the material
multiple charge states of the defects
e.g. formation of Ti\(^{3+}\) polaron states

→think of the FE oxide as a wide band gap SC
Position of \(E_F\) determines defect charge states and defect formation enthalpies
The $V_{\text{Pb}}$ related lifetime $\tau_2$

First principle total energy calculations predict [1] several stable charge states of $V_{\text{Pb}}$

The existence of $V_{\text{Pb}}$-$V_{\text{O}}$ bound complexes is unlikely (endothermic, negative binding energies), However:

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Vacuum annealing

![Graph showing lifetime and intensity vs. anneal temperature for 4% Nb:PZT](image)

- Lifetime $\tau_1$: 160 ps
- Lifetime $\tau_2$: 280 ps
- Intensity, $I$: 10% - 50%
- Anneal. Temp. [K]: 200 - 1200 K
- $E_A$: 1.2 ± 0.3 eV
$V_0$ trapping coefficient

(1) extremely high conc.
\[ k = \mu C \]
\[ e.g.: \mu \text{ für Si: } \mu(V_{si}^+) : 6 \times 10^{13} \text{ s}^{-1} \]
\[ \mu(V_{si}^0) : 6 \times 10^{14} \text{ s}^{-1} \]
\[ \mu(V_{si}^-) : 5 \times 10^{15} \text{ s}^{-1} \]

(2) The charge is not 2+!
\textbf{Ti} as a transition metal has empty 3d states
charge compensation
Temperature dependent trapping coefficient of positrons for different charge states

Calculation for semiconductors
Temperature dependant positron lifetimes

Fe – O(V) charge transfer above 150 K

Positive charge state

Neutral charge state
Mössbauer spectra of $^{57}\text{Fe}$ (0.5%):Pb$_1$(Zr$_{54}$Ti$_{46}$)$_1$O$_3$ at different temperatures

- **Doublet:** Fe – O$_v$ dipoles
- **Isomery shift:** charge state Fe$^{3+}$ (in agreement with ESR)

- **Sextet:** low spin relaxation
- **No magnetic interaction because the large average distance between Fe atoms:** distribution is homogenous
Interpreting the donor doping effects

- $\tau_2$ is clearly associated to $V_{Pb}$
- $\tau_2$ gradually increases from 255 to 305 ps with the dopant concentration
- For high donor concentrations the position of $E_F^\uparrow$, which energetically favours associated $V_O^- V_{Pb}$ vacancy complexes
- Defect concentrations are generally so high that saturation occurs
  - $\tau_1$ is stable at ~170 ps which corresponds to single $V_O$
- Further evidence that $\tau_1$ is not the bulk lifetime but associated with $V_O$ comes from vacuum annealing experiments (defect formation enthalpy is about $E\sim 1 eV$)
  - The charge state of $V_O$ is probably not 2+
Microstructural Effects

SEM images provided by H. Kungl
Oxygen Tracer Diffusion

18O Ion Implantation

Annealing of the samples / Electrical fatigueing depth profiling of the 18O Tracer by means of SIMS or NRA 18O(p,γ)19N E_{res} : 151.2 ± 0.05 keV

However using poly samples GB contributions are apparent!
18O-tracer Diffusion Experiments

Thermal indiffusion of 18O is possible
However, limited temperature range (200-400°C)
Alternative: 18O ion implantation

Depth profiles include several fast diffusive components
D ranges from $7 \times 10^{-19}$ - $2 \times 10^{-15}$ cm$^2$/sec

Separation of the components
Electric cycling mediated diffusion is in progress
$^{18}$Oxygen Tracer Diffusion

thermal $^{18}$O exchange indiffusion $400^\circ C$ for 3 hrs. 2psi

\[
\text{erf} \left( \frac{x}{2(Dt)^{0.5}} \right)
\]

0.02% natural abundance
Principle of SIMS measurement

primery ions (O or Cs)

secondary ions to analyse

optic

SIMS crater

sputtering

sample
SIMS $^{18}$O depth profiles in PZT (Pb-Zr-Ti-O) ferroelectric samples
Activation enthalpies and chemical surface reaction for O in PZT

Activation energy $E_A$: $0.68 \pm 0.07$ eV

Recombination energy $E_R$: $1.2 \pm 0.1$ eV

Diffusion coefficient $D_{GB}$

Diffusion coefficient $D_{bulk}$

Reaction rate $k$
Oxygen Implantation

\[1^8\text{O Conc. [arb. units]}\]

\[5 \text{ keV}
\]
FWHM: 14 nm
\[x_0: 9 \text{ nm}\]

\[10 \text{ keV}
\]
FWHM: 25 nm
\[x_0: 15 \text{ nm}\]

\[15 \text{ keV}
\]
FWHM: 33 nm
\[x_0: 22 \text{ nm}\]

\[20 \text{ keV}
\]
FWHM: 44 nm
\[x_0: 28 \text{ nm}\]

\[30 \text{ keV}
\]
FWHM: 64 nm
\[x_0: 41 \text{ nm}\]
Summary and Conclusions

- **PAS** clearly shows that La as well as Nb doping yields to the saturation of lifetime component $\tau_2$, supposedly belonging to $\tau(V_{Pb}) \sim 300$ps
  - both dopants produce single Pb vacancies
  - we suggest the existence of associated $V_{Pb}V_O$ vacancies in undoped samples, However $\tau(V_{Pb}V_O)^0 < \tau(V_{Pb})^2$
  - as $\tau_2$ saturates, $\tau_{\text{bulk}}$ disappears, and $I_2$ drops, $\tau_1$ can be attributed to $\tau(V_O) \sim 155$ ps
  - consequently the dopant also creates $V_O$
  - Surprisingly $V_O^{2+}$ are easily detectable with **PAS**