Defects and porosity in zirconia-based nanomaterials

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Talk outline

- Introduction/motivation.
- Experiments.
- Results and discussion.
- Conclusions.
- Acknowledgements.
Introduction / motivation

Zirconia (zirconium dioxide, ZrO$_2$):

- A wide band gap ($E_g \approx 5 – 7$ eV) semiconductor exhibiting a number of useful thermal, electrical, mechanical and chemical properties,
- A basic constituent of many functional materials.
- Doping with proper metal cations benefits in
  - stabilisation of high temperature tetragonal (t-) or cubic (c-) phases of zirconia down to room temperature,
  - optimisation of other material characteristics.

There is still continuing interest in investigations of zirconia nanomaterials doped with various metal cations.
Open-volume defects in doped zirconia nanomaterials.

**Nanopowders** – GBs related defects dominate.

- Small open-volume defects:
  - vacancy-like misfit defects situated along GBs ($\tau_v \approx 0.19$ ns),
  - open volumes at intersections of three GBs (triple points, $\tau_t \approx 0.4$ ns).
- Nano- and mesopores – still incomplete knowledge about these structural elements.
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Nanoceramics.
- metal cation vacancies inside grains ($\tau_V \approx 0.17$ ns).
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**Nanoceramics.**
- metal cation vacancies inside grains ($\tau_V \approx 0.17$ ns).

**Positron annihilation spectroscopy (PAS)** – efficient tool of defects investigations into doped zirconia nanopowders and nanoceramics.
Scope of the present talk

- Present talk is focused on zirconia nanopowders and ceramics doped with the MgO and CeO$_2$.
- PAS techniques: the conventional positron lifetime (PLT) spectrometry and the variable-energy slow-positron beam spectroscopy were employed.
- Complementary techniques – electron microscopy, mass-density measurements.
Experiments

Samples

- **ZrO$_2$ nanopowders** (dopants Mg$^{2+}$, Ce$^{4+}$):
  - Initial nanopowders – co-precipitation from water solutions of appropriate salts taken in stoichiometric compositions (developed and performed by Donetsk branch).
  - Calcination @ $T_c$ (1 h in air).
  - Characterisation of nanoparticle size by TEM or XRD (mean particle size between 10 and 20 nm).
  - Compaction of calcined nanopowders into pellets (≈15 mm radius and ≈2 mm thickness) – uniaxial pressure $P$ of 5 kbar.
Experiments

Samples

- **ZrO$_2$ nanopowders** (dopants Mg$^{2+}$, Ce$^{4+}$):
- **Nanoceramics** obtained by sintering compacted ZrO$_2$ nanopowders @ $T_s = 1500$ °C (1 h in air).
Nanopowders of tetragonal ZrO$_2$ doped with 3 mol.% Y$_2$O$_3$ (t-YSZ) and 3mol.% Cr$_2$O$_3$, prepared by the similar technique, were involved for comparison.
Experiments

Positron lifetime (PLT) spectroscopy

- A BaF$_2$ fast–fast delayed-coincidence spectrometer (Becvar et al., 2000).
- Measurements were conducted at room temperature in air.
- Positron/positronium lifetimes up to $\approx 140$ ns were investigated.
Experiments

Slow-positron beam spectroscopy

Magnetically guided positron beam SPONSOR @ HZDR (Anwand et al., 1995, 2012):

- range of positron energies $E$ from 0.03 to 35 keV,
- single HPGe detector measurements (1.05 keV FWHM, $5 \times 10^5$ counts in 511 keV peak),
- shape parameters, $S(E)$ and $W(E)$,
- relative positronium $3\gamma$-fractions, $F_{3\gamma}(E)$. 
Results & discussion

PLT spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_{\text{OPS},1}$ [ns]</th>
<th>$R_1$ [nm] $^a)$</th>
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$^a)$ Pore radii estimated from Wada & Hyodo model, corrected for ortho-para conversion in air.
Results & discussion

PLT spectroscopy
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PLT spectroscopy

Ortho-Ps data on pressure-compacted nanopowders (lifetimes $\tau_{oPs,i}$, pore radii $R_i$ and rel. intensities $I_{Ps}$)

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a) Pore radii estimated from Wada & Hyodo model, corrected for ortho-para conversion in air.

In t-YSZ and MgSZ, two ortho-Ps components observed:
- the larger pores ($R_2 \approx 5$ nm),
- the smaller pores ($R_1 \approx 0.6$ nm).
Results & discussion

PLT spectroscopy

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a) Pore radii estimated from Wada & Hyodo model, corrected for ortho-para conversion in air.

In CeSZ, only shorter oPs component could be revealed:

- the smaller pores ($R_1 \approx 0.6$ nm) are evidenced.
Results & discussion

PLT spectroscopy

- In zirconia-based nanopowders doped with several other metal cations (monoclinic ZrO$_2$, cubic YSZ, ZrO$_2$ doped with Eu$^{3+}$, Gd$^{3+}$, Lu$^{3+}$), similar two-component pattern like the $t$-YSZ and MgSZ case were observed, too:
  - $t_{oPs,1} \approx 7.5$ ns, $I_{p.o.,1} \approx 0.7 \%$, $R_1 \approx 0.6$ nm;
  - $t_{oPs,2} \approx 70$ ns, $I_{p.o.,2} \approx 7.5 \%$, $R_2 \approx 4.5$ to $8.5$ nm, originated likely from cavities between primary nanoparticle aggregates.
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Aggregation of primary nanoparticles (Ito et al., 1999):

- A pore among primary nanoparticles
- A pore among nanoparticle aggregates
Results & discussion

PLT spectroscopy

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Aggregation of primary nanoparticles (Ito et al., 1999):

Aggregates of 14 particles reported in YSZ.
Results & discussion

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Aggregates – equal-sized rigid spherical particles:

Packing factor $\xi$: $\xi = 0.75$ – dense packing,
  $\xi = 0.64$ – random close packing,
  $\xi \approx 0.55$ – random loose packing.
Results & discussion

PLT spectroscopy

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Aggregates – equal-sized rigid spherical particles:

$L = 4 \ R_{oPs,2} / 3$ – the mean free path in a hole, then number of particles forming an aggregate is $\approx 7$. 

from $\tau_{oPs,2}$
Results & discussion

PLT spectroscopy

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Aggregates – equal-sized rigid spherical particles:

However:

- terms ‘equal-sized’, ‘rigid’ or ‘spherical’,
- randomness of packing.
Results & discussion

PLT spectroscopy

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- CeSZ case is an exclusion:
  - the larger pores likely do not occur (aggregation of primary nanoparticles does not take place?).
Results & discussion

Measured mass densities

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<th>ρ/ρ_th (^a)</th>
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<td>2.922 (5)</td>
<td>0.478</td>
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<td>0.37</td>
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<td>0.450</td>
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\(^a\) ρ\(_{th}\) = 6.11 g/cm³ adopted.

MgSZ, t-YSZ ceramics: ρ ≈ 5.8 g/cm\(^{-3}\) (≈ 95 % of ρ\(_{th}\)).

Pressure-compacted nanopowders – random close- (or loose)-packed aggregates of dense packed nanoparticles.
Further evidence for absence of the large pores in CeSZ (contrary to MgSZ and YSZ, RESZ):

- electron microscopy,
- slow-positron beam spectroscopy.
Results & discussion

TEM observation on nanopowders

Aggregates of primary nanoparticles: more visible in MgSZ than in CeSZ.
Results & discussion

TEM observation on nanopowders

MgSZ

CeSZ

Larger pores: more visible in MgSZ than in CeSZ. Pore sizes: reasonable consistency with PLT data.

smaller pores (1 to 2 nm);

larger pores (4 to 5 nm, seen in MgSZ, not in CeSZ).
Results & discussion

Slow-positron beam spectroscopy

Vanishing of $F_{3\gamma}$ in the bulk – the strongest evidence of an absence of large pores in CeSZ:
Results & discussion

Slow-positron beam spectroscopy

Vanishing of $F_{3\gamma}$ in the bulk – the strongest evidence of an absence of large pores in CeSZ:

![Graph showing the vanishing of $F_{3\gamma}$ for different samples]
In zirconia nanopowders doped with yttria, magnesia, two kinds of pores with radii estimated as $R_1 \approx 0.6$ nm and $R_2 \approx 4.5$ to 8.5 nm.

The larger pores are likely cavities between small nanoparticle aggregates (tentatively $\approx 7$ primary nanoparticles).

The $\text{ZrO}_2 + \text{CeO}_2$ seems to contain the smaller pores only, but not the large ones, pointing toward an absence of significant particle aggregation. This system thus may receive some attraction for applications when particle aggregation is unwanted.
Acknowledgements

- **ICPA-18 Organisers:** hospitality and providing a possibility to present results at this Conference.

- **Finance funding:** Czech Science Foundation (project P108/12/G043), Nat. Acad. Sci. of Ukraine (project 89/12-H).

- **The four Institutions:** supporting members of teams in fruitful co-operation on working-out this Contribution.

Thank you for kind listening!
Swan song
Relative positronium (Ps) 3γ-fractions, \( F_{3\gamma}(E) \)

\[
F_{3\gamma}(E) = R(E) - R_{\text{ref}} ,
\]

where

\[
R(E) \equiv \frac{V(E)}{A_{2\gamma}(E)} ,
\]

\[
R_{\text{ref}} \equiv \frac{V_{\text{ref}}}{A_{2\gamma,\text{ref}}} .
\]

‘\( \text{ref} \)’ state – bulk reference material with no Ps formation, measured with the same setup,

\( A_{2\gamma}(E) , A_{2\gamma,\text{ref}} \) – 511 keV peak areas,

\( V(E) , V_{\text{ref}} \) – background subtracted areas left to 511 keV peak (480 – 500 keV region).
Schematic view of packing of rigid spherical particles

Particle aggregate

Particle

$V_p = \frac{\pi}{6} d^3$

Particle aggregate

$V_{ag} = \frac{4\pi}{3} R^3$

Packing factor $\xi$:

$\xi = 0.75$ – dense packing,

$\xi = 0.64$ – random close packing,

$\xi \approx 0.55$ – random loose packing.

$N_p = \frac{\xi \cdot V_{ag}}{V_p}$

$2r \approx 2R \cdot (\sqrt{2} - 1)$

from $\tau_{0Ps,2}$