Positron annihilation studies of zirconia doped with metal cations of different valence

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Introduction & motivation

- Zirconia (ZrO_2) – basic constituent of a variety of industrial materials purposed especially for operation at high temperatures.
- Stabilisation of high-temperature phases of zirconia is needed: appropriate metal oxide is introduced as solid solution into zirconia host lattice.
- Frequently, yttria (Y_2O_3) is used to produce yttria-stabilised zirconia (YSZ), e.g. addition of ≈ 3mol.% of yttria givespartially stabilised *tetragonal* phase (*t*-YSZ).
- Stoichiometry violation due to stabiliser addition (differences in valences of doping and host metal atoms) ⇒ a huge amount of oxygen vacancies and related defect complexes.

Introduction & motivation

Current trends in prospecting new zirconia-based materials:

- Examination of new *stabilising agents* which could replace the 'traditional', but relatively expensive yttria: e.g. magnesia (MgO), ceria (CeO_2).
- *Ternary oxide systems*: other metal oxide is introduced together with the stabiliser agent into the host lattice to reach better material properties (smaller particle size, hindering unwanted grain growth, ...).
- Use of *nanopowders* as starting substances for manufacturing of zirconia-based materials by pressure compaction, sintering, etc. (defects associated to grain boundaries(GBs)

⇓

Positron annihilation spectroscopy (PAS) may provide valuable knowledge about open-volume defects in zirconia-based materials.

Introduction & motivation

Systematical PAS investigations of YSZ nanomaterials were carried out within Prague – Dresden-Rossendorf – Donetsk collaboration (to appear in *Defects and Diffusion Forum,* 2012):

- Pressure compacted nanopowders (mean particle size of ≈ 20 nm or less), sintered ceramics.
- Binary and ternary (with chromia) systems.
- Conventional PAS (lifetime, coincidence Doppler broadening techniques).
- Slow-positron implantation spectroscopy (SPIS).

Present contribution:

- new conventional PAS investigation on pressure-compacted nanopowders of magnesia- and ceria-stabilised zirconia (MgSZ and CeSZ, respectively) and several other ZrO_2-based binary and ternary oxide nanosystems;
- SPIS on *t*-YSZ and *t*-YSZ with small chromia additive (*t*-YSZC).

Experimental – samples (Donetsk)

Pressure-compacted nanopowders

- Initial nanoparticles: co-precipitation from water solutions of salts.
- Calcination at 500 - 600 °C for 1 h.
- Uniaxial compression under P = 500 MPa into disks of ≈15 diameter and 5 mm thickness.
- TEM and XRD characterisations prior and after pressure compaction (phase composition, mean particle size).

Experimental – samples (Donetsk)

Pressure-compacted nanopowders

Abbrev.	Composition	Phase	Experiment
MgSZ	ZrO_2 + 10 mol.% MgO	*t*	conventional
CeSZ	ZrO_2 + 12 mol.% CeO_2	*t*	PAS
Z0Y	pure ZrO_2	*m*	
Z3Y	ZrO_2 + 3 mol.% Y_2O_3	*t*	conventional
Z3C	ZrO_2 + 3 mol.% Cr_2O_3	*t*	PAS
Z3Y0.3C	ZrO_2 + 3 mol.% Y_2O_3 + 0.3 mol.% Cr_2O_3	*t*	
Z3Y0.7C	ZrO_2 + 3 mol.% Y_2O_3 + 0.7 mol.% Cr_2O_3	*t*	
t-YSZ	ZrO_2 + 3 mol.% Y_2O_3	*t*	SPIS
t-YSZC	ZrO_2 + 3 mol.% Y_2O_3 + 0.7 mol.% Cr_2O_3	*t*	

Experimental – samples (Donetsk)

Sintering of *t*-YSZ and *t*-YSZC

- Sequential sintering at temperatures T_S = 600, 700, 800 and 900 °C in air.
- Slow cooling down to room temperature in the furnace swittched off.
- Each annealing step followed by a SPIS measurement.

Experimental – apparatus & data acquisition

Conventional PAS

- Positron lifetime (LT) technique:
  BaF_2 analog or digital spectrometers (≈ 140÷160 ps FWHM, $>10^7$ counts per spectrum).
- Coincidence Doppler broadening (CDB) technique:
  HPGe – HPGe coincidence apparatus (1.1 keV FWHM at γ 511keV, $>10^8$ counts per spectrum.

Experimental – apparatus & data acquisition

SPIS

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

- positron energy range E_+ = (0.03 – 35 keV),
- single HPGe detector measurements (1.05 keV FWHM, 10^6 counts),
- shape parameters S and W,
- relative positronium (Ps) fractions F are calculated as

$$F(E_+) = \frac{R(E_+) - R(\mathrm{no\,Ps})}{R(\mathrm{lowest}\,E_+) - R(\mathrm{no\,Ps})} \quad , \quad R(E_+) \equiv \frac{V(E_+)}{A_{2\gamma}(E_+)} \quad ,$$

where

$A_{2\gamma}$ – 511 keV peak area,

V – counts in 480 – 500 keV region,

'no Ps' state – *t*-YSZC at E_+ > 20 keV.

Results – LT measurements in compacted nanopowders

Sample	*d* [nm]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_{oPs} [ns]	I_{Ps} [%]
MgSZ	11	261(3)	52(2)	441(4)	41(2)	18.1(2)	6.0(5)
CeSZ	9.1	254(4)	22(1)	408(4)	76(1)	19.7(4)	2.0(5)
Z0Y	23	187(3)	42(2)	377(4)	48(2)	31(2)	9.6(4)
Z3Y	18	174(4)	27(2)	373(3)	63(2)	30(2)	9.7(4)
Z3C	9	178(3)	16(1)	374(3)	84(1)		
Z3Y0.3C	18	191(3)	32(1)	381(2)	69(1)		
Z3Y0.7C	15	191(3)	26(1)	390(2)	74(1)		

Results – LT measurements on binary YSZs

Sample	*d* [nm]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_{oPs} [ns]	I_{Ps} [%]
MgSZ	11	261(3)	52(2)	441(4)	41(2)	18.1(2)	6.0(5)
CeSZ	9.1	254(4)	22(1)	408(4)	76(1)	19.7(4)	2.0(5)
Z0Y	23	187(3)	42(2)	377(4)	48(2)	31(2)	9.6(4)
Z3Y	18	174(4)	27(2)	373(3)	63(2)	30(2)	9.7(4)
Z3C	9	178(3)	16(1)	374(3)	84(1)		
Z3Y0.3C	18	191(3)	32(1)	381(2)	69(1)		
Z3Y0.7C	15	191(3)	26(1)	390(2)	74(1)		

Saturated positron trapping:

- vacancy-like misfit defects situated along GBs – $\tau_1 \approx 180 \div 200$ ps,
- triple points at junctions of three GBs – $\tau_2 \approx 400$ ps,
- nanopores (voids) of ≈ 2 nm size – $\tau_{oPs} \approx 30$ ns, voids between primary particles.

Results – LT measurements on MgSZ and CeSZ

Sample	*d* [nm]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_{oPs} [ns]	I_{Ps} [%]
MgSZ	11	261(3)	52(2)	441(4)	41(2)	18.1(2)	6.0(5)
CeSZ	9.1	254(4)	22(1)	408(4)	76(1)	19.7(4)	2.0(5)
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Z3Y0.7C	15	191(3)	26(1)	390(2)	74(1)		

Saturated positron trapping:

- vacancy-like defects and triple points (τ_1 and τ_2), but with larger lifetimes than in binary YSZs,
- nanopores of ≈ 0.9 nm size, i.e. smaller than in YSZ, reasonably correlated with smaller particle size.

Results – LT measurements in nanopowders containing chromia

Sample	*d* [nm]	τ_1 [ps]	I_1 [%]	τ_2 [ps]	I_2 [%]	τ_{oPs} [ns]	I_{Ps} [%]
MgSZ	11	261(3)	52(2)	441(4)	41(2)	18.1(2)	6.0(5)
CeSZ	9.1	254(4)	22(1)	408(4)	76(1)	19.7(4)	2.0(5)
Z0Y	23	187(3)	42(2)	377(4)	48(2)	31(2)	9.6(4)
Z3Y	18	174(4)	27(2)	373(3)	63(2)	30(2)	9.7(4)
Z3C	9	178(3)	16(1)	374(3)	84(1)		
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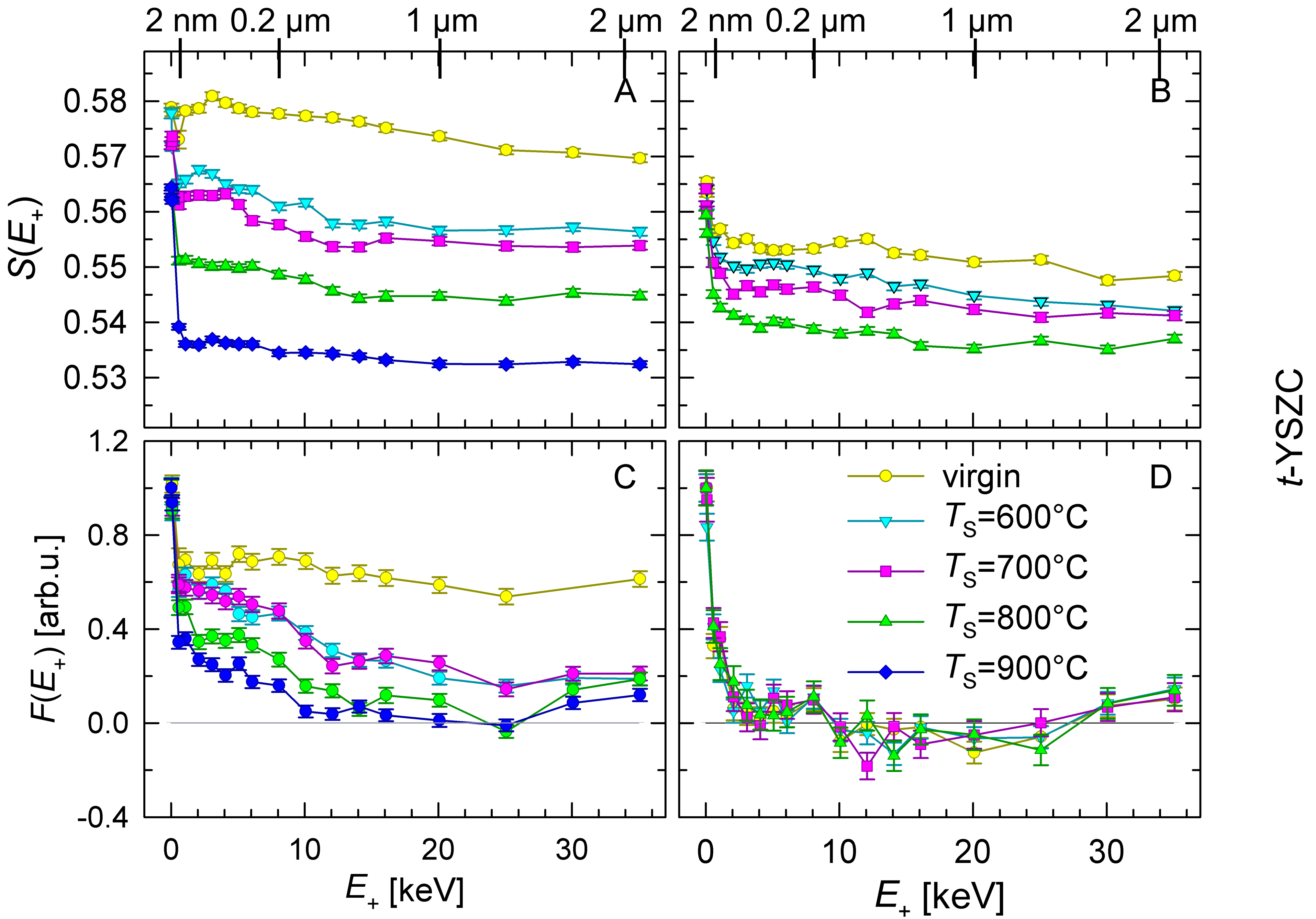
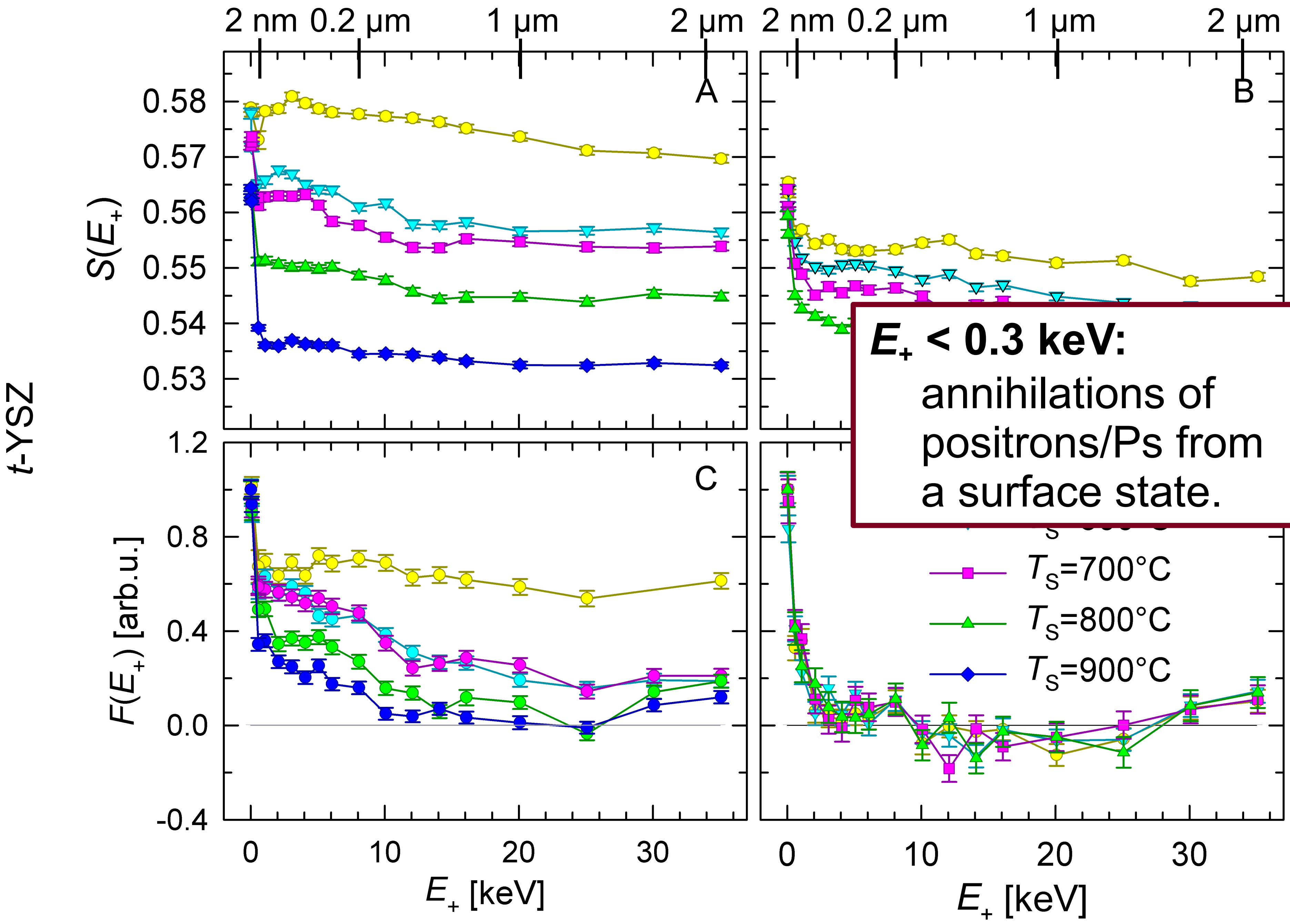
No Ps detected even for small amounts of Cr_2O_3 (0.3 mol.%) → evidence for Cr segregation along GBs.

Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS

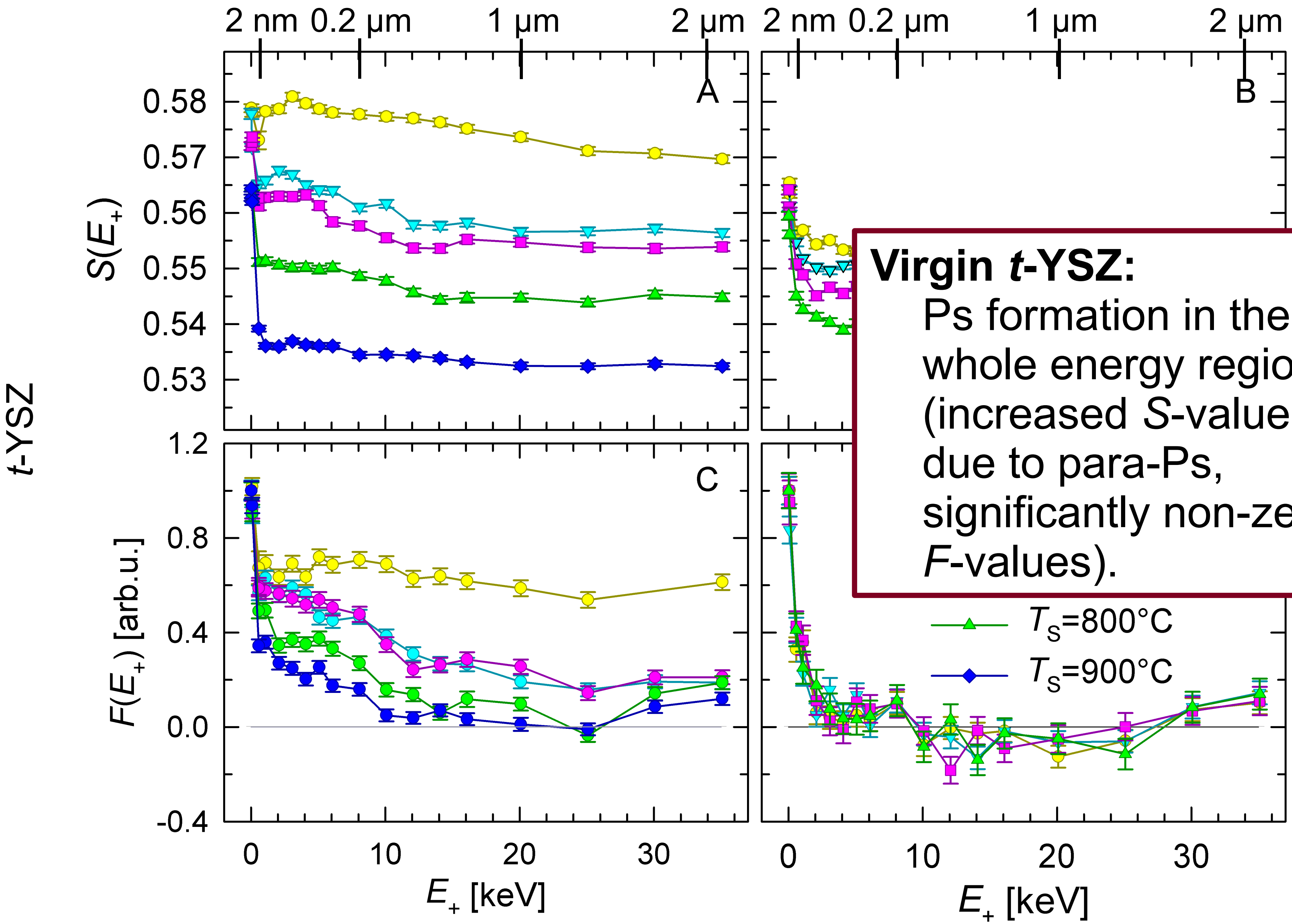


Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS



***E_+* < 0.3 keV:**
annihilations of
positrons/Ps from
a surface state.

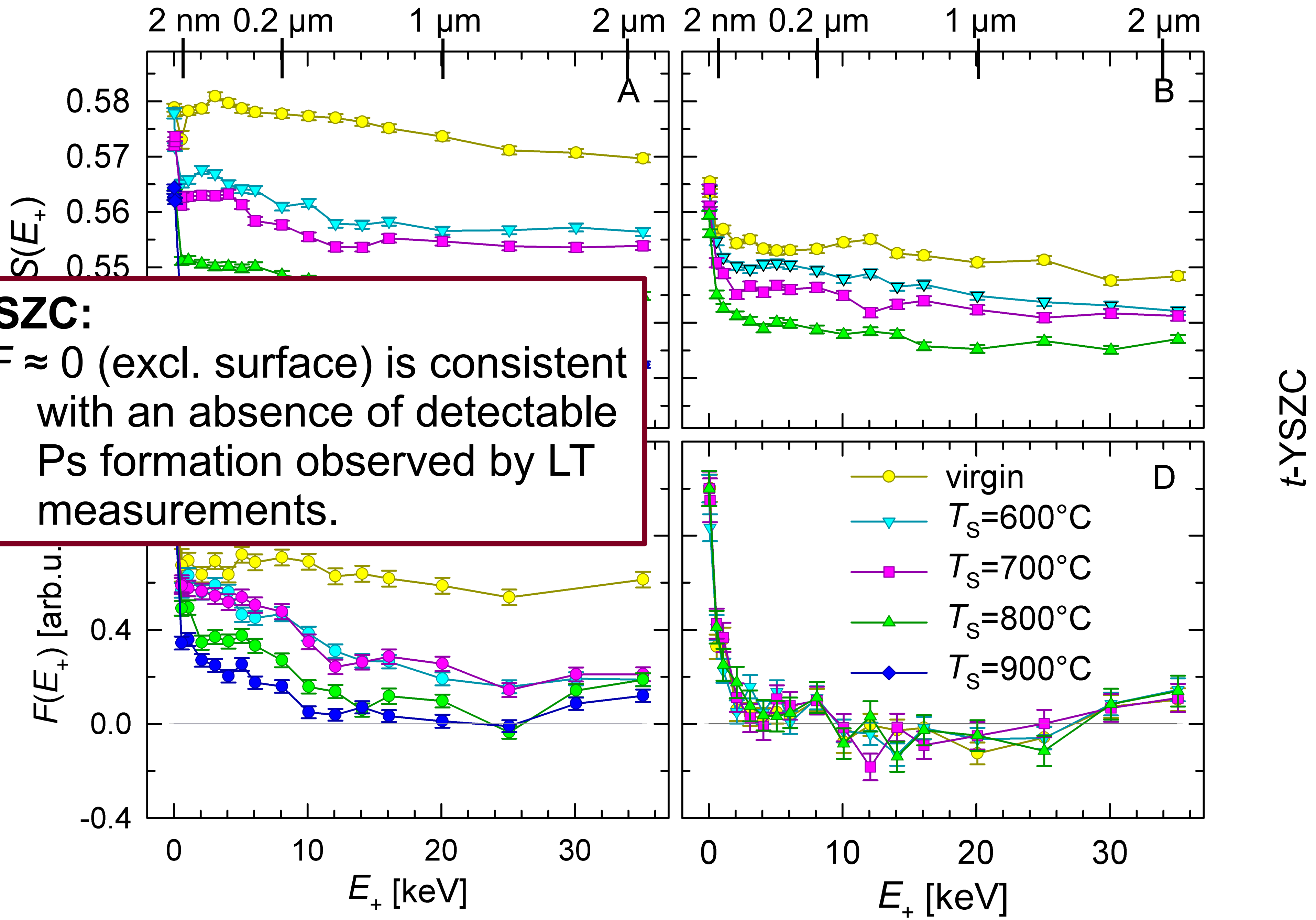
Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS



Virgin *t*-YSZ:

Ps formation in the whole energy region (increased *S*-values due to para-Ps, significantly non-zero *F*-values).

Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS



***t*-YSZC:**

F ≈ 0 (excl. surface) is consistent with an absence of detectable Ps formation observed by LT measurements.

Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS

$E_+ > 20$ keV ($\bar{z} > 1$ µm):

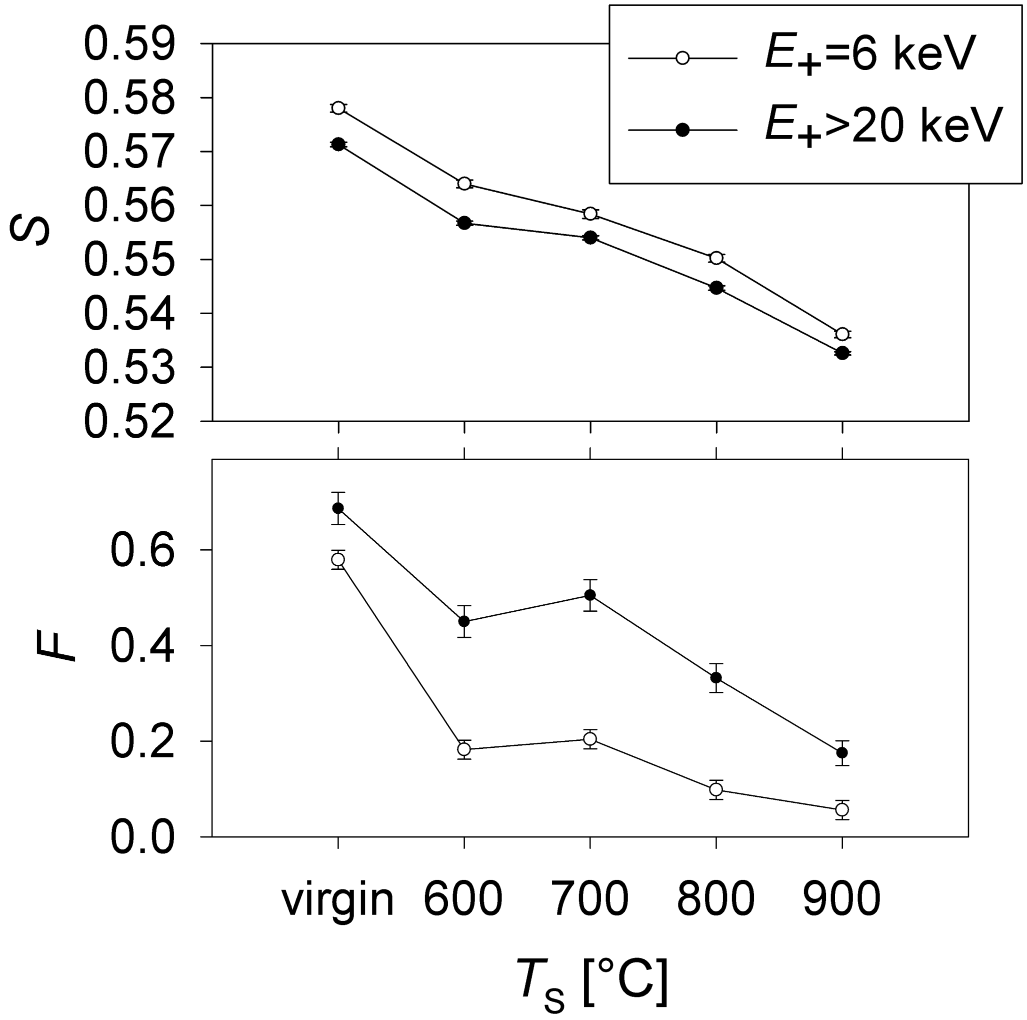
- Plateau-like pattern of *S*- and *F*- values exhibiting
  - a well-pronounced decrease of *S*-parameters in both materials,
  - a decrease of *F*-values in *t*-YSZ

  with increased T_S , which results from sintering-induced grain growth and disappearance of pores.

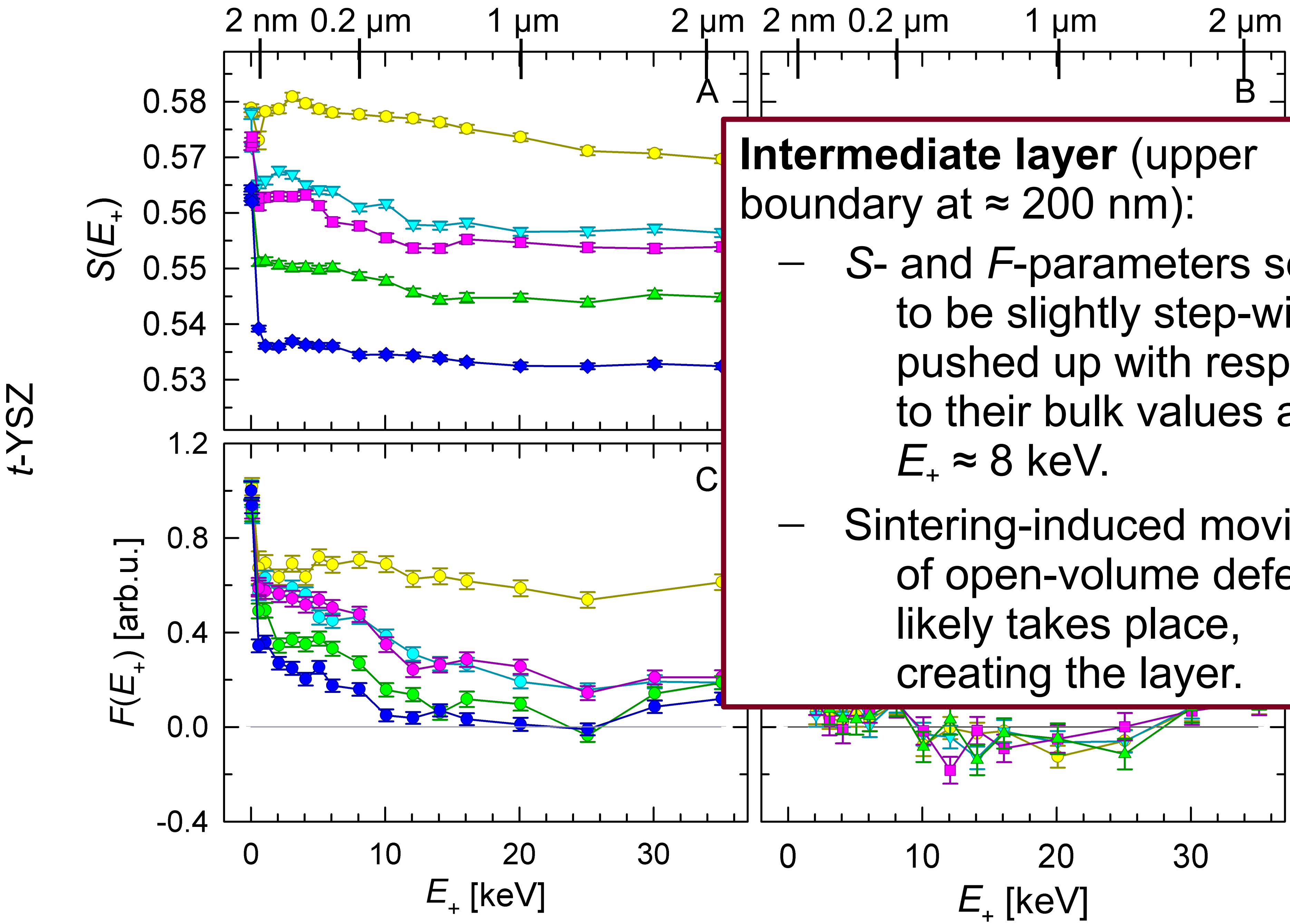
- Two sintering stages seem to be distinguished:
  - $T_S \approx 600$ °C – disappearance of pores in *t*-YSZ dominates, as indicated by a strong decrease of *F*-parameters,
  - $T_S > 800$ °C – disappearance of small open-space defects (vacancy-like defects, triple points) is reflected by a significant decrease of *S*-values accompanied by a relatively small decrease of *F*-parameters.

Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS

S- and *F*-parameters as functions of T_S:



Results – sintering of *t*-YSZ and *t*-YSZC monitored by SPIS



Intermediate layer (upper boundary at ≈ 200 nm):

- *S*- and *F*-parameters seem to be slightly step-wise pushed up with respect to their bulk values at E_+ ≈ 8 keV.
- Sintering-induced moving of open-volume defects likely takes place, creating the layer.

Summary

- Positrons in YSZ, CeSZ and MgSZ pressure-compacted nanopowders annihilate from trapped states:
  - vacancy-like misfit defects situated along GBs,
  - triple points.
- In all samples, except for those containing Cr_2O_3 , Ps is formed indicating an existence of nm pores between primary particles.
- Sintering of *t*-YSZ compacted nanopowders leads to disappearance of pores followed by grain growth.

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