Sintering of zirconia-based nanomaterials studied by variable- energy slow-positron beam

I. Prochazka[1], J. Cizek[1], O. Melikhova[1], W. Anwand[2], G. Brauer[2], T. E. Konstantinova[3], I. A. Danilenko[3]

[1] *Charles University in Prague, Faculty of Mathematics and Physics, Department of Low Temperature Physics, Prague, Czech Republic*
[2] *Institut für Strahlenphysik, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany*
[3] *Donetsk Institute for Physics and Engineering named after O. O. Galkin, Nat. Acad. Sci. of Ukraine, Donetsk, Ukraine*

SLOPOS
Munich 2013

13th Internat. Workshop on Slow Positron Beam
Techniques and Applications, 15–20 September 2013,
TU München

Talk schedule

- ☐ Introduction
- ☐ Experiments
- ☐ Results & discussion
- ☐ Concluding remarks

Introduction

Zirconia (ZrO_2) – advantageous thermal, electronic, mechanical and chemical properties:

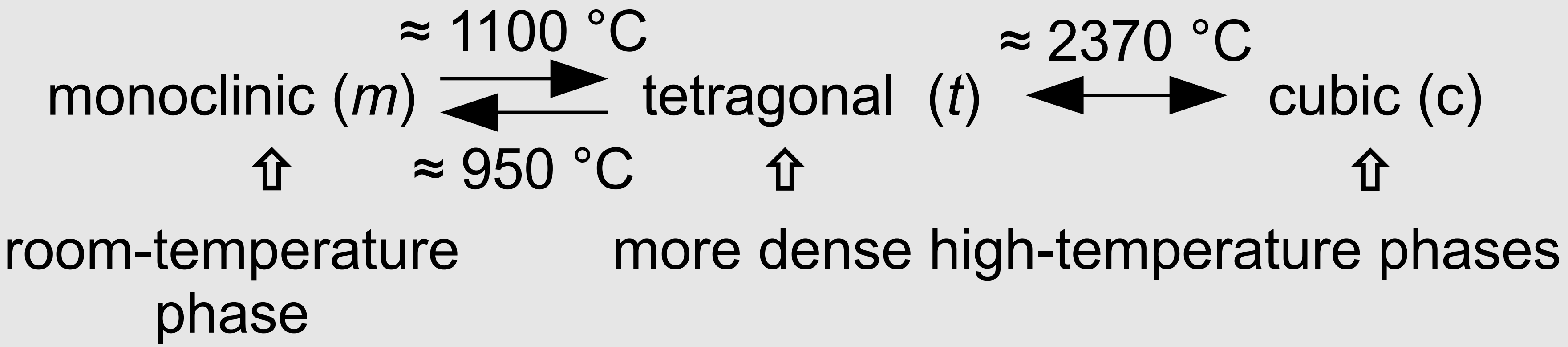
- ☐ a high melting point (2750 °C),
- ☐ a low thermal conductivity,
- ☐ a good high-*κ* dielectricity,
- ☐ a low electronic conductivity,
- ☐ a good oxygen ionic conductivity at increased temperatures,
- ☐ a high hardness combined with a reasonable fracture toughness,
- ☐ a good resistance to corrosion and wear.

Zirconia – a substance widely used in practice,
e.g. in ceramic industry,

Introduction

Zirconia polymorphism

Pure zirconia:



$$\text{monoclinic } (m) \underset{\approx 950\ ^\circ\text{C}}{\overset{\approx 1100\ ^\circ\text{C}}{\rightleftharpoons}} \text{tetragonal } (t) \xleftrightarrow{\approx 2370\ ^\circ\text{C}} \text{cubic (c)}$$

⇧ room-temperature phase

⇧ ⇧ more dense high-temperature phases

Repeated passage of the *pure* zirconia through the *t* ↔ *m* phase-transition temperature may lead to a deterioration of mechanical properties of the material.

⇩

A stabilisation of the high-temperature zirconia cubic and tetragonal phases is required if zirconia is to be used at temperatures above ≈ 1000 °C.

Introduction

Yttria-stabilised zirconia (YSZ)

Yttria (Y_2O_3) dispersed in the zirconia lattice as a solid solution is known to be a good phase stabiliser:

- ≈ 8 mol. % of Y_2O_3 is sufficient to keep the *c*-phase of zirconia down the room temperature (*c*-YSZ),
- ≈ 2÷3 mol. % of Y_2O_3 may stabilise the zirconia *t*-phase below ≈ 1000 °C (*t*-YSZ).

Introduction

Zirconia ceramics

Sintering of fine powders – an efficient method of manufacturing ceramics:

- activation of mass transfer resulting in
  - grain growth and
  - disappearance of pores;
- key driving parameters are
  - sintering temperature, T_s ,
  - grain size, d,
  - diffusivity of constituents;
- potentially depth-dependent phenomena.

Introduction

Zirconia nanomaterials

Use of nanopowders as the starting materials for manufacturing ceramics by sintering:

- a more efficient sintering,
- a positive influence on resulting porosity,
- a better mixing on the atomic scale even for substances which are immiscible under normal conditions,
- enhanced role of grain boundaries (GBs) compared to more ordinary coarse-grained materials.

Introduction

Zirconia nanomaterials

Various open-volume structures appear in zirconia-based nanomaterials:

- ☐ open-volume defects associated to GBs (vacancy-like misfit defects, triple points),
- ☐ pores of a few-nanometer size between nanocrystallites (typically ≈ 10÷30 nm particle size),
- ☐ vacancy-like defects resulting from the stoichiometry violation by dopant – oxygen vacancies (V_O) and V_O-related complexes,
- ☐ potential migration of impurity atoms toward GBs.

⇓

Zirconia-based nanomaterials – a challenge for positron annihilation spectroscopy (PAS).

Introduction

The aims of the present study:

The potentially depth-dependent sintering-induced diffusion processes in zirconia-based nanomaterials

ZrO_2 + 3 mol.% Y_2O_3 , ZrO_2 + 3 mol.% Y_2O_3 + 1 mol.% Cr_2O_3

were studied for different T_S using slow-positron implantation spectroscopy (SPIS).

Experiments

Samples

Nanopowders

- ☐ ZrO_2 + 3 mol.% Y_2O_3 (Z3Y),
  ZrO_2 + 3 mol.% Y_2O_3 + 1 mol.% Cr_2O_3 (Z3Y1C),
- ☐ method of co-precipitation from water solutions of respective salts taken in stoichiometric proportions,
- ☐ calcination at 500 °C/2 h in air,
- ☐ uniaxial pressure compaction (500 Mpa) – disks of ≈10 mm diameter, ≈3 mm thickness,
- ☐ XRD characterisation of nanopowders:
  - *t*-phase,
  - d = 17.0 ± 0.9 nm (Z3Y) , 13 ± 1 nm (Z3Y1C).

Experiments

Samples

Sintering

- Step-by-step sintering at 600, 700, 800, 900, 1100, 1300 and 1500 °C/1 h in air with subsequent controlled cooling down to room temperature,
- SPIS measurement after each step.

Experiments

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, 5×10^5 counts),
- shape parameters $S(E_+)$ and $W(E_+)$,
- relative positronium (Ps) 3γ fractions $F(E_+)$ - Wu Y.C., 2011.

$$F(E_+) = R(E_+) - R_{\mathrm{noPs}} \quad , \quad R(E_+) \equiv \frac{V(E_+)}{A_{2\gamma}(E_+)} \quad , \quad R_{\mathrm{noPs}} \equiv \frac{V_{\mathrm{noPs}}}{A_{2\gamma,\mathrm{noPs}}} \quad ,$$

where

$A_{2\gamma}$ – 511 keV peak area,

V – counts in 480 – 500 keV region,

'noPs' state – *t*-YSZC at E_+ > 20 keV.

Experiments

SPIS

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

- positron energy range $E_+ = (0.03 – 35\ \text{keV})$,
- single HPGe detector measurements (1.05 keV FWHM, 5×10^6 counts),
- shape parameters $S(E_+)$ and $W(E_+)$,
- relative positronium (Ps) 3γ fractions $F(E_+)$ - Wu et al., 2011.

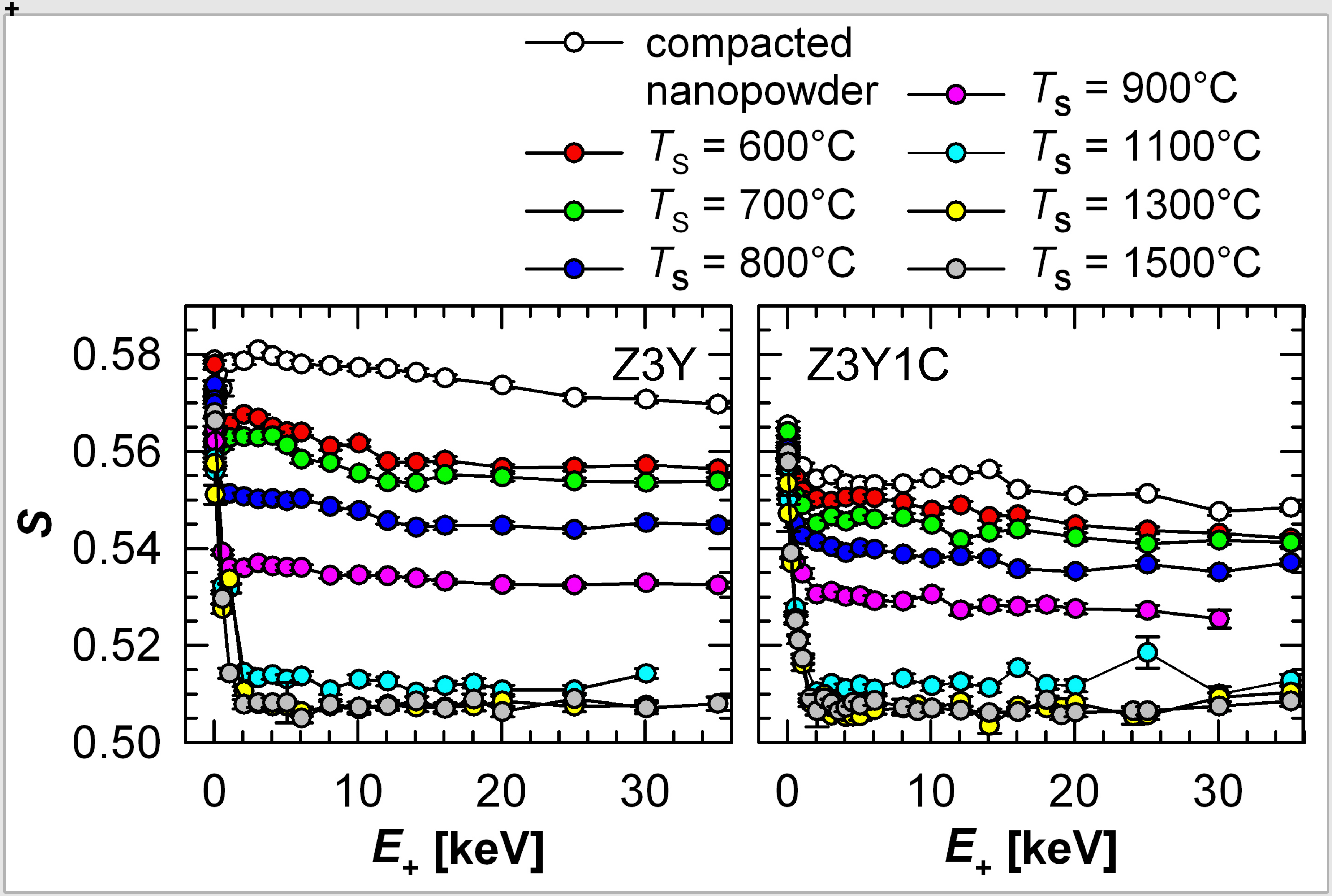
$$F(E_+) = R(E_+) - R_{\text{noPs}} \quad , \quad R(E_+) \equiv \frac{V(E_+)}{A_{2\gamma}(E_+)} \quad , \quad R_{\text{noPs}} \equiv \frac{V_{\text{noPs}}}{A_{2\gamma,\text{noPs}}} \quad ,$$

where

'noPs' state – Z3Y1C (a complete suppression of Ps formation due to Cr cations segregated close to GBs (Melikhova et al., 2012).

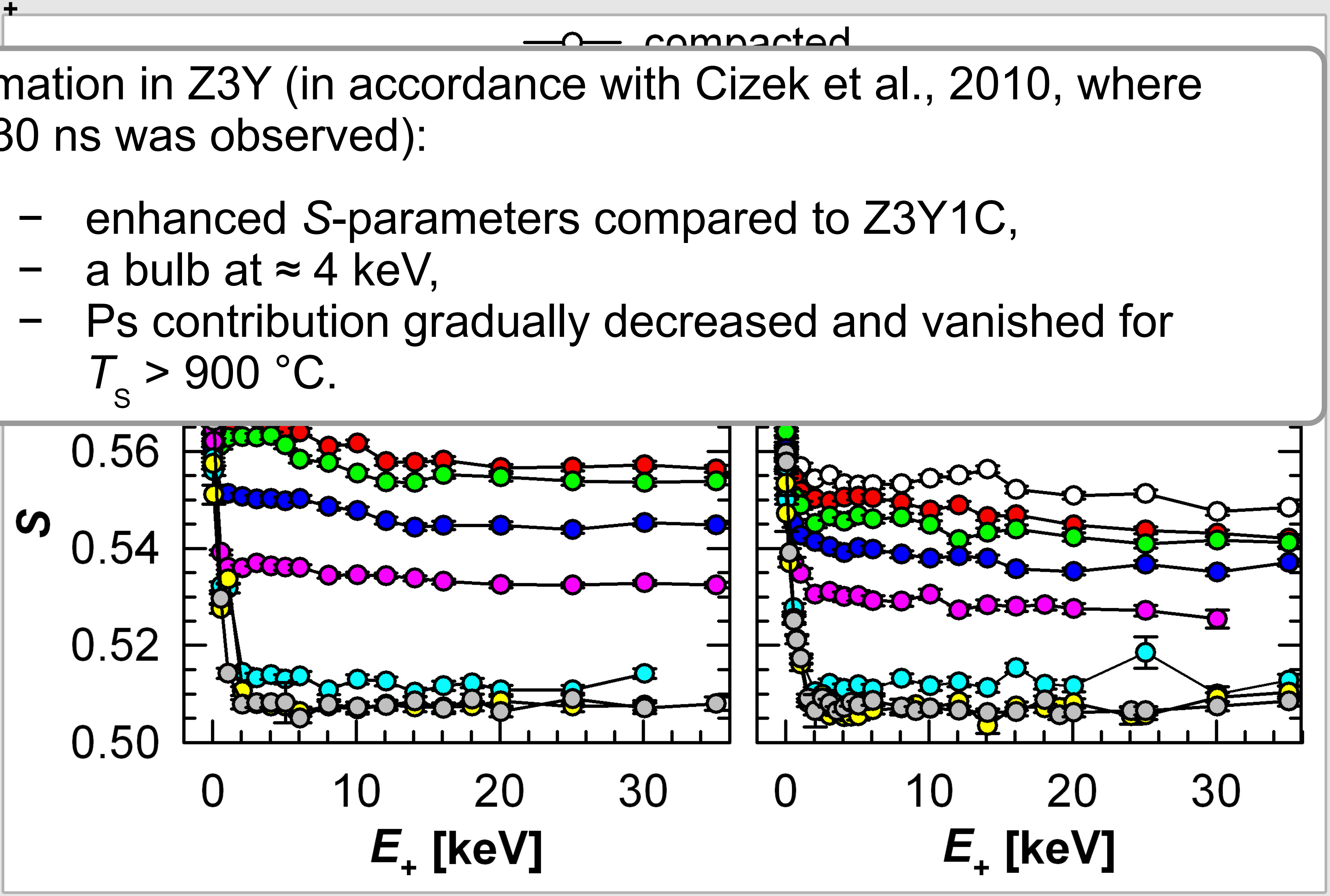
Results & discussion

S vs E_+



Results & discussion

S vs E_+

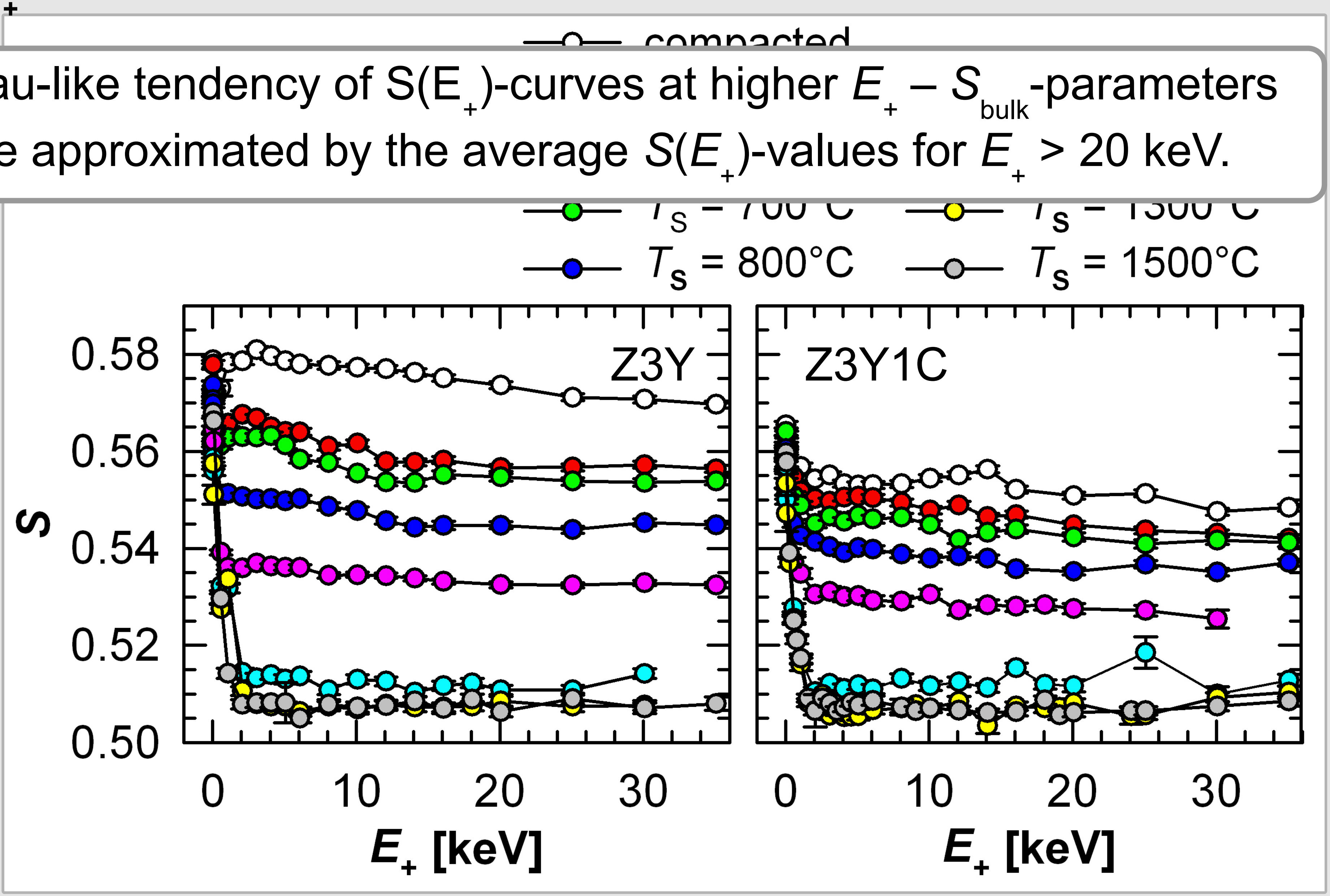


Ps formation in Z3Y (in accordance with Cizek et al., 2010, where $\tau_{oPs} \approx 30$ ns was observed):

- enhanced *S*-parameters compared to Z3Y1C,
- a bulb at ≈ 4 keV,
- Ps contribution gradually decreased and vanished for $T_S > 900$ °C.

Results & discussion

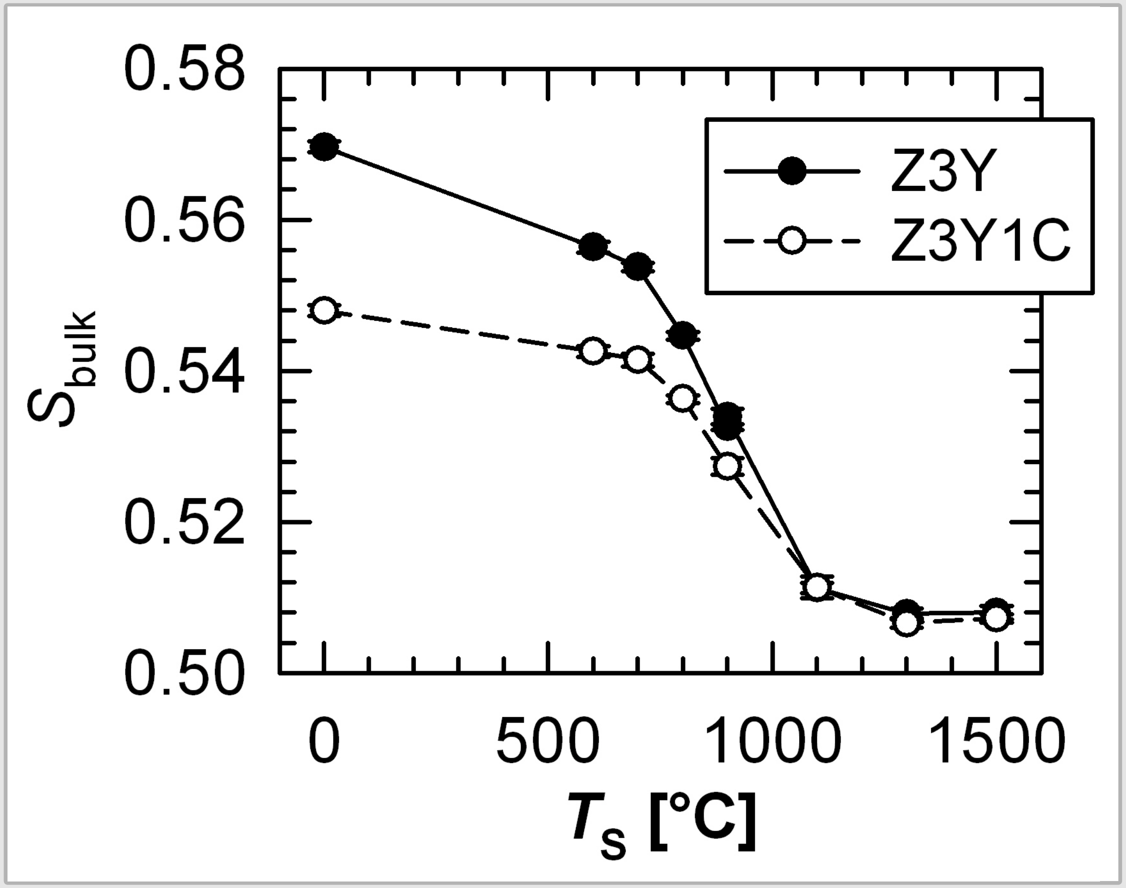
S* vs *E_+



Plateau-like tendency of S(E_+)-curves at higher E_+ – S_{bulk}-parameters may be approximated by the average $S(E_+)$-values for E_+ > 20 keV.

Results & discussion

S_{bulk} vs T_S



Results & discussion

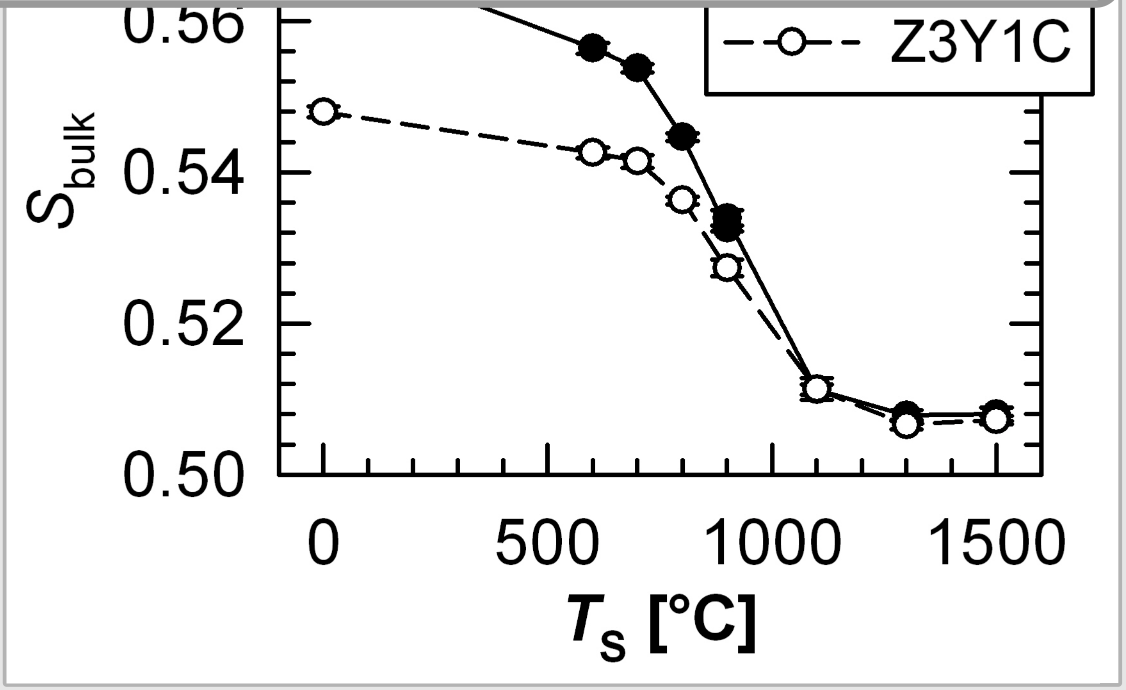
S_{bulk} vs T_S

Two kinds of sintering-induced changes leading to a decrease of S_{bulk} with T_S:

(1) disappearance of pores (diminishing of Ps contribution),
(2) grain growth (a decrease in the concentration of GB-associated defects)

In Z3Y, both (1) and (2) were observed.

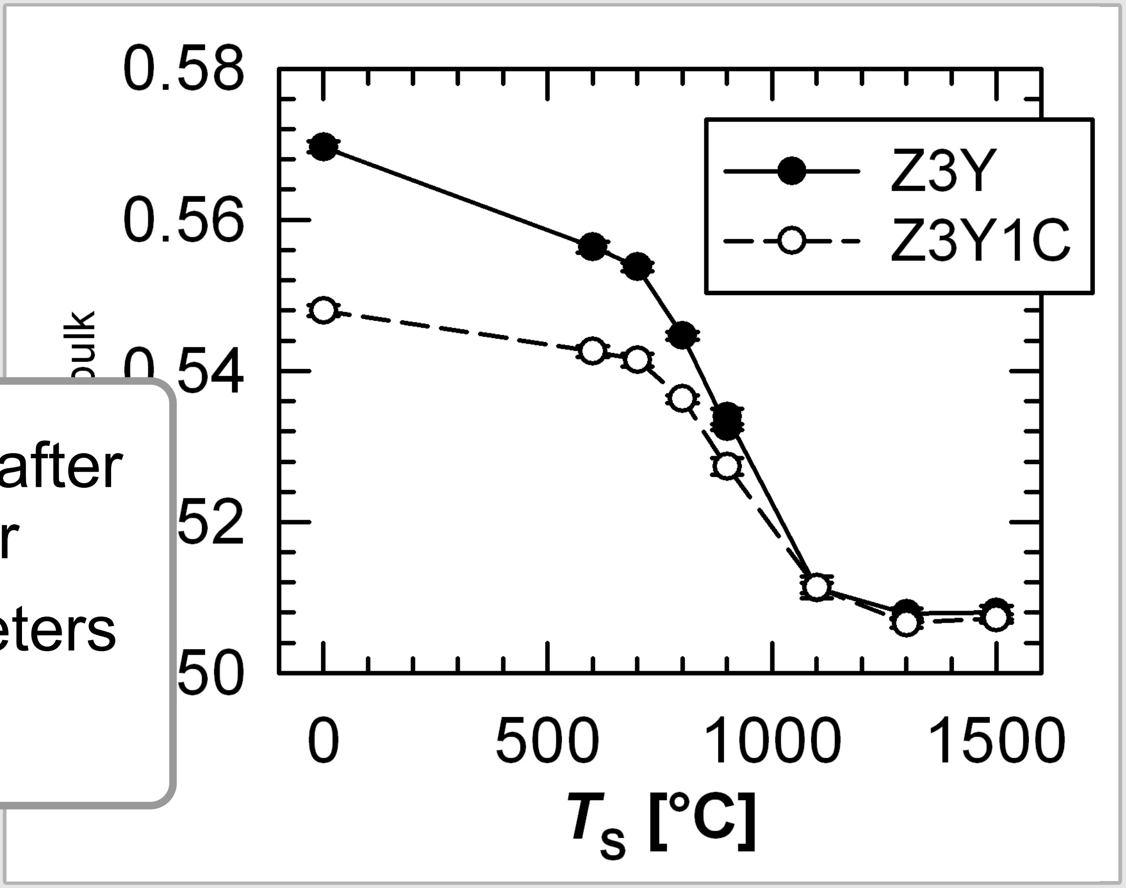
In Z3Y1C, only (2) can be seen.



Results & discussion

S_{bulk} vs T_S

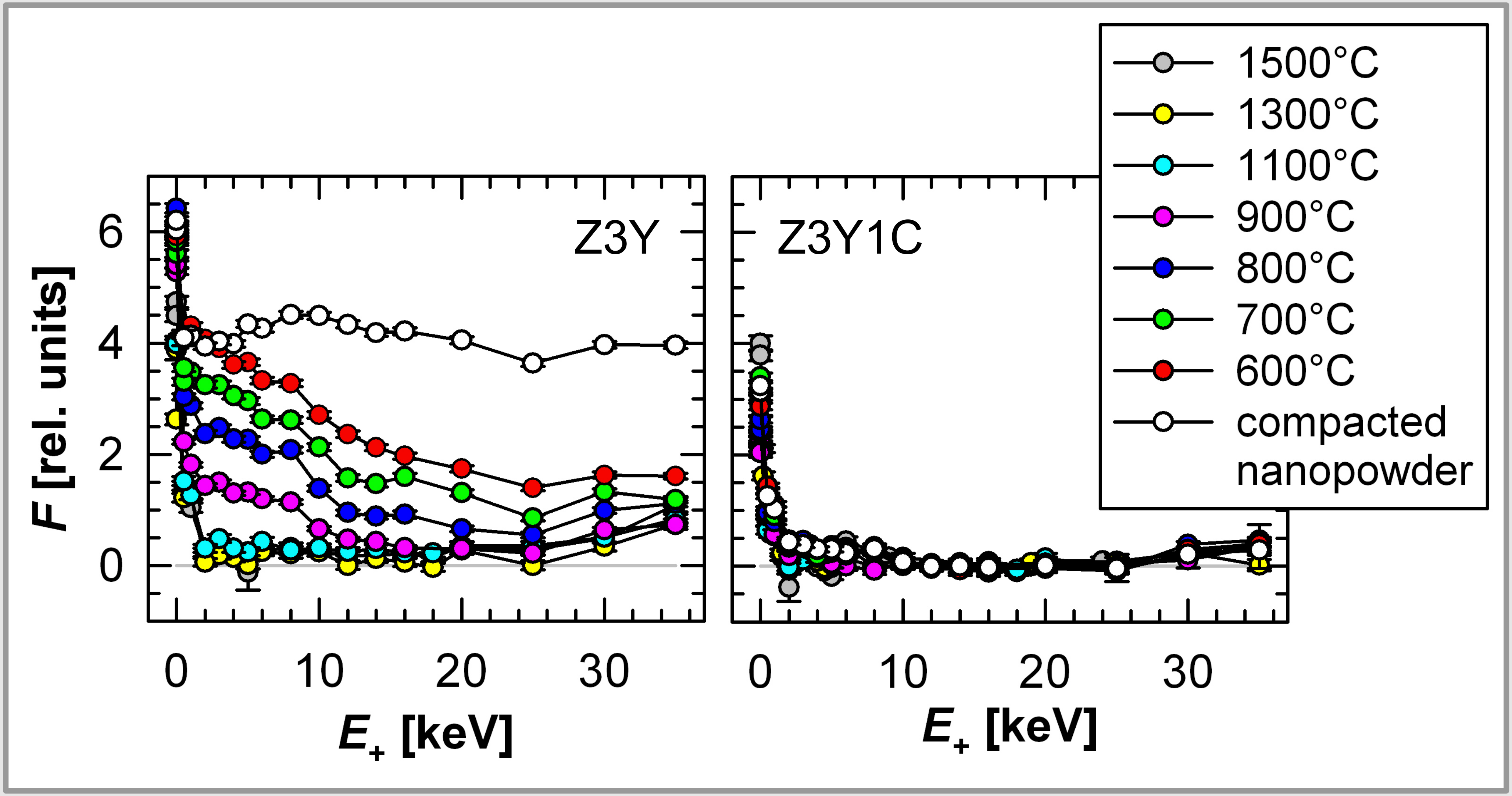
An excess in S_{bulk}-values in Z3Y compared to Z3Y1C can be regarded as a measure of porosity.



Porosity is essentially removed after sintering at T_S ≈1000 °C. Further (slight) decrease of S_{bulk}-parameters is solely due to grain growth.

Results & discussion

F vs E_+

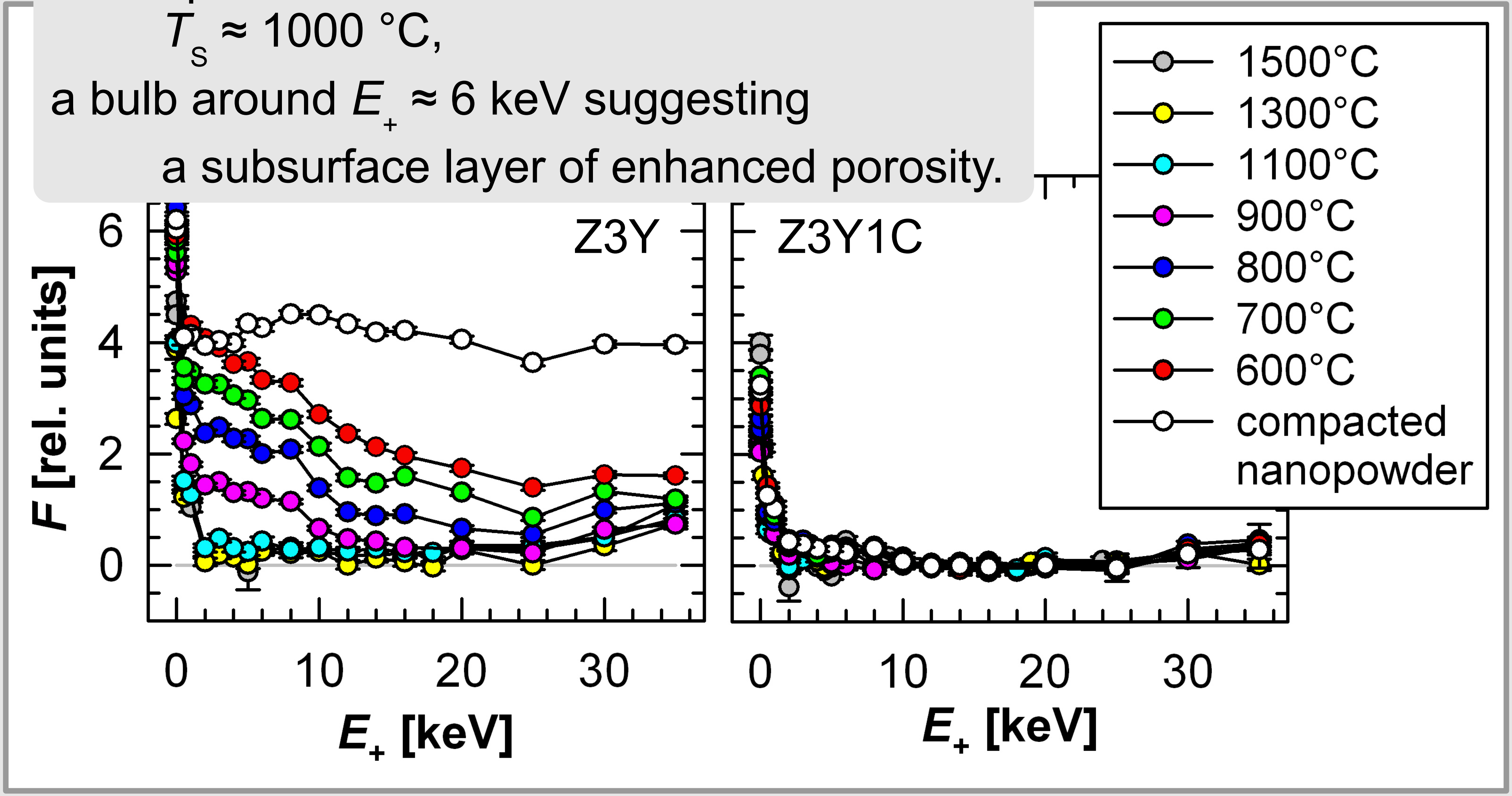


Results & discussion

F vs E_+

A sharp decrease of the bulk *F*-values above $T_s \approx 1000$ °C,

a bulb around $E_+ \approx 6$ keV suggesting a subsurface layer of enhanced porosity.



Concluding remarks

Present experimental data shows that pronounced effects could be revealed by the depth profiling of sintering-induced microstructure changes by means of SPIS:

> A subsurface layer of enhanced porosity was identified which is likely a manifest of sintering-activated diffusion driven from sample interior toward its surface.

Structure inhomogeneities in the nanograined materials on a 100 nm scale, on the other hand, give positron behaviour a rather complicated nature. To reach a more detailed understanding of experimental data, different models of diffusion mechanisms should be taken into account.

Acknowledgements

Financial support:

- The Czech Science Foundation – P108/11/1396,
- Charles University in Prague – programme UNCE (OM),
- National Academy of Science of Ukraine – 89/12-H.

SLOPOS Organizers – for providing time and space for this presentation

Thanks the auditory for patient listening