Defects in yttria-stabilised zirconia:
a positron annihilation study

J. Cizek[1], **O. Melikhova**[1], **J. Kuriplach**[1], **I. Prochazka**[*,1], **T. E. Konstantinova**[2],
and **I. A. Danilenko**[2]

[1] Department of Low Temperature Physics, Faculty of Mathematics and Physics,
   Charles University in Prague, V. Holesovickach 2, 180 00 Prague 8, Czech Republic
[2] Donetsk Institute of Physics & Engineering NASU, Donetsk, Ukraine

High-resolution positron lifetime and coincidence Doppler-broadening measurements on the yttria-stabilised zirconia compacted nanopowders, differing in phase, stabiliser content and preparation conditions, are reported. The nature of defects observed in these materials is discussed on the basis of available experimental data and their comparison with theoretical calculations. It is concluded that positrons annihilate mainly in vacancy-like defects at grain boundaries and in larger open-volume defects associated with triple points. A fraction of positrons annihilating in mesopores of ≈ 2.5 nm diameter was also detected.

1 Introduction   Zirconia-based materials made of nanometer grain size powders offer an exceptional combination of advantageous thermal and mechanical properties, which makes these materials attractive for various industrial applications like, for example, heat-resistance structural and functional ceramics, solid oxide fuel cells and oxygen sensors. However, a stabilisation of the tetragonal and cubic phases of zirconia, e.g. by an addition of trivalent yttrium oxide is needed when high-temperature applications of zirconia are required. Such an addition leads to a formation of a certain amount of defects in the ZrO_2 lattice. These defects in turn influence properties of yttria-stabilised zirconia (YSZ) and the nature and the role of defects introduced by stabilisation is in need of a detailed elucidation in order to taylor zirconia-based materials of required properties. Moreover, the role of grain boundaries (GBs) which constitute a large volume fraction in the compacted nanopowders should be taken into consideration, too. Porosity is another important property of interest in these materials. It is then obvious that positron annihilation spectroscopy (PAS) is a promising tool for microstructure studies of zirconia-based nanomaterials. Despite of several PAS investigations on YSZs published earlier, see e.g. [1–4], there is still a rather poor understanding and ambiguous explanations of the observed PAS data.

   In the present Contribution, high-resolution positron lifetime (PL) measurements on the YSZ compacted nanopowder materials, differing in phase, stabiliser content and conditions of preparation, are reported. These measurements are supplemented by a coincidence Doppler broadening (CDB) investigation using two HPGe detectors. The nature of defects observed in these materials is discussed on the basis of available experimental data and their comparison with the theoretical calculations of positron lifetimes and high-momentum parts of Doppler profiles, performed [5] within the framework of the atomic superposition method considering appropriate vacancy-type defect configurations.

---

*   Corresponding author: e-mail: ivanp@mbox.troja.mff.cuni.cz

2 Experiment *Specimens*   The three zirconia-based nanosize powders were investigated in the present work: pure ZrO_2 (denoted below as Z0Y, monoclinic phase), ZrO_2+3 mol.% Y_2O_3 (Z3Y, tetragonal) and ZrO_2+8 mol.% Y_2O_3 (Z8Y, cubic). The mean grain size of starting nanopowders was determined by XRD and TEM observations as 23.2, 17.6 and 15.6 nm, respectively. Powders were calcinated at 700 °C and pressed at room temperature into tablets of 15 mm diameter and 5 mm thickness. The three different pressures of 250, 500 and 1000 MPa were applied. In addition, a monocrystalline ZrO_2+3 mol.% Y_2O_3 (Z3Yx, tetragonal) and a pure ZrO_2 compacted powder (Z0Ym, monoclinic, mean grain size of 40÷50 nm, calcinated at 1100 °C and pressed under 1000 MPa) were also studied in the present work. Further details of materials preparation were given elsewhere [6].

Measurements   A 1.3 MBq of $^{22}Na_2CO_3$ (iThemba Labs) sealed between MylarC foils (Dupont) of 4 µm thickness was used as a positron source. The source was sandwiched between two pieces of the material studied. A fast-fast mode of the PL spectrometer described in [7] was employed in the present work. The spectrometer exhibited the time resolution of 0.163 ns (fwhm). All the above zirconia-based materials were characterised by means of the PL method and at least 10^7 counts were accumulated in each PL spectrum. The spectra were analysed using the maximum likelihood procedure [7]. For the CDB measurements, a spectrometer equipped with the two HPGe detectors [8] having an energy resolution of 1.05 keV at 511 keV was utilised. The Z0Y, Z3Y, Z8Y nanopowders, compacted under 1000 MPa, and the Z3Yx monocrystal were studied by means of CDB. About 10^8 counts were accumulated in each CDB spectrum. A well-annealed iron served as a reference material for determining ratios of CDB profiles. All the PL and CDB measurements were performed in air at ambient temperature.

3 Results and discussion   Measured positron lifetime spectra were decomposed into up to four components (positron source contribution and para-positronium component were subtracted). The resulting lifetimes τ_i and intensities I_i are summarised in Table 1. CDB profiles measured in the present work were related to that of the well-annealed iron reference specimen and the ratios obtained are shown in Fig. 1.

Table 1   Positron lifetimes and intensities measured in the present work (standard deviations are given in parentheses in units of the last significant digit).

Material	Pressure [MPa]	τ_1 [ns]	I_1 [%]	τ_2 [ns]	I_2 [%]	τ_3 [ns]	I_3 [%]	τ_4 [ns]	I_4 [%]
Z0Y	250	0.185(2)	43(2)	0.370(4)	46(2)	1.9(1)	1.8(1)	31(2)	6.3(3)
	500	0.187(3)	42(2)	0.377(4)	48(2)	1.8(1)	1.5(1)	31(2)	5.7(3)
	1000	0.193(2)	44(2)	0.374(4)	44(2)	2.0(1)	2.3(1)	31(2)	6.0(3)
Z3Y	250	0.181(2)	33(2)	0.381(3)	58(2)	2.0(2)	1.2(1)	31(2)	5.4(3)
	500	0.174(3)	27(2)	0.373(3)	63(2)	1.6(1)	1.4(1)	30(2)	5.9(3)
	1000	0.180(4)	25(2)	0.369(3)	63(2)	1.7(1)	2.0(1)	28(2)	7.1(3)
Z8Y	250	0.187(3)	30(2)	0.375(4)	60(3)	2.0(2)	1.2(1)	30(2)	5.5(3)
	500	0.185(3)	30(2)	0.365(4)	60(2)	2.2(1)	2.1(1)	26(2)	5.0(3)
	1000	0.197(3)	31(2)	0.378(3)	58(2)	2.2(2)	1.6(1)	31(2)	5.9(3)
Z0Ym	1000	0.182(1)	83(1)	0.397(4)	17(1)			~20	<1
Z3Yx	–	0.165(2)	80(5)	0.249(9)	20(5)				

Observed lifetimes τ_1 for Z0Y, Z3Y and Z8Y samples, see Table 1, seem to resemble those calculated for the Zr-vacancy or Zr-vacancy+O-vacancy complexes in Ref. [5]. Despite of this similarity, however, the origin of the τ_1-component can hardly be fully explained by positron trapping in vacancy-like defects *inside* grains. First, a low equilibrium concentration of Zr vacancies takes place in these materials at room temperature. Moreover, nanocrystalline grain size of compacted powders under study leads to a significant volume fraction of GBs. Positrons thermalised inside grains are expected to reach easily
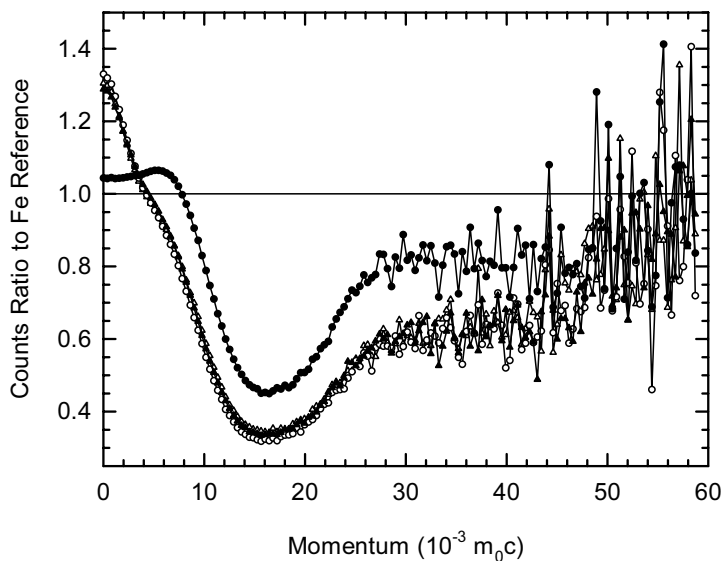
Fig. 1 Observed ratios of DB profiles to that of well-annealed iron: Δ - Z0Y (ZrO$_2$, monoclinic, powder), ○ - Z3Y (ZrO$_2$+3 mol.% Y$_2$O$_3$, tetragonal, powder), ▲ - Z8Y (ZrO$_2$+8 mol.% Y$_2$O$_3$, cubic, powder), ● - Z3Yx (ZrO$_2$+3 mol.% Y$_2$O$_3$, tetragonal, monocrystal). All powder samples were pressed under 1000 MPa.

GBs because of a weak role of positron trapping due to a low positron binding to defects as suggested by theoretical calculations [5]. Hence we argue that positrons annihilate mainly in vacancy-like defects at GBs (τ_1-component) and in larger open-volume defects associated with triple points at GBs (τ_2-component). This interpretation differs from that of Ref. [2] in which positron trapping mainly inside grains is supposed. On the other hand, a similar point of view as our one can be found in Refs. [3, 4]. Below we shall give further supporting arguments. First, observed intensity ratios I_2:I_1 for the Z0Y, Z3Y and Z8Y samples are significantly increased in the two yttria-added materials compared to the pure zirconia one and this trend is almost independent of applied pressure. The smaller the grains, the better chance for a positron to reach GB by diffusion motion and get trapped there. It is shown in Fig. 2 that the ratios I_2:I_1 correlate roughly linearly with the reciprocal values of the above mean grain size d. Such behaviour can be understood as resulting from the proportionality of the concentration of triple points and vacancy-like defects at GBs to $\sim d^{-3}$ and $\sim d^{-2}$, respectively. Moreover, the enhanced role of positron trapping in defects at GBs in the compacted nanopowders, compared to the Z3Yx monocrystal, is clearly indicated by the observed CDB profiles in the low-momentum region, see Figure 1. In the high-momentum part, there is virtually no difference in the CDB-ratio curves observed for various specimens (Fig. 1). Such behaviour demonstrates a shape similarity of the yttrium and zircon contribution in this momentum region [5]. On the other hand, a non-monotonic behaviour of observed τ_1-values in dependence of the yttria content (Table 1) suggests that the nature of the τ_1-component is complex and a minor contribution from positron trapping in vacancy-like defects inside grains may take place.

An appreciable amount of mesopores in Z0Y, Z3Y and Z8Y specimens is indicated by the observed ortho-positronium τ_4-components of ≈ 6 % intensity, see Table 1. The pore size and volume fraction in these three materials seem not to depend on applied pressure, thus suggesting that the compressibility of powders reaches already saturation in the range of pressures applied. Assuming the semi-empirical correlation between the ortho-positronium lifetime and the pore size, proposed by Ito et al. [9], we can estimate the pore diameter in Z0Y, Z3Y and Z8Y specimens to be $\approx 2.5 \div 3.0$ nm for $\tau_4 \approx 30$ ns which is considerably smaller than the mean grain size of starting nanopowders. Similarly as in Ref. [1], this component can be attributed to mesopores among primary grains. Longer lifetime components (of apparently weak intensity) could not be detected in the present work. Thus the existence of the larger pores among secondary particles formed by aggregation of primary grains remains an open question and a matter of further investigations. Obviously, the absence of the porosity component, exhibited by the lifetime spectrum of Z0Ym specimen (Table 1), is to be related probably to a greater grain size leading to a smaller pore concentration. Note that an analogous effect, i.e. an absence of this mesopore component at in-

creased grain size, was also observed in Ref. [1] for specimens compacted under considerably lower pressure of 50 MPa.

In summary, positrons annihilate in the compacted nanopowder zirconia-based materials, studied in the present work, mainly at GBs: (i) in vacancy-like defects at grain surface and (ii) in the larger open-volume defects associated with triple points. A portion of positrons forms positronium and annihilates also in mesopores. PL parameters turn out to be correlated with the composition, structure and preparation conditions, demonstrating the method as an effective tool for microstructural investigations on YSZ nanomaterials. In particular, sensitivity of measured PL parameters to the defect type (vacancy-like defects, triple points, mesopores) and mean grain size may be outlined. To get a more detailed structural knowledge on these YSZ materials, it appeared advantageous to supplement PL data with CDB measurements.
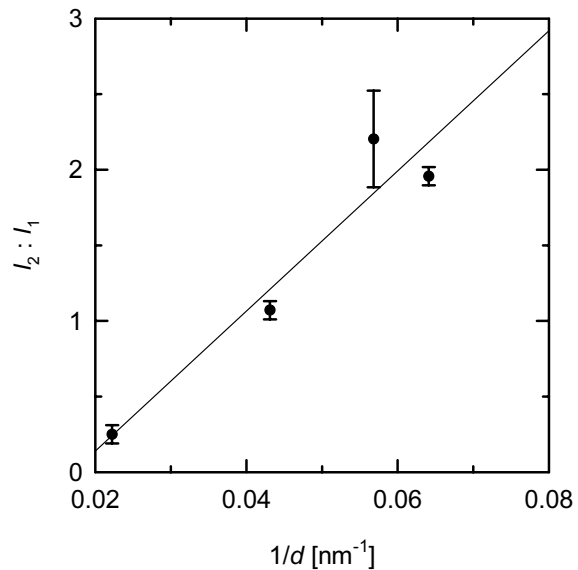
Fig. 2 The dependence of $I_2{:}I_1$ on mean grain size d obtained for nanopowder specimens.

References

[1] K. Ito, Y. Yagi, S. Hirano, M. Miyayama, T. Kudo, A. Kishimoto, and Y. Ujihira, J. Ceram. Soc. Jpn. **107**, 123 (1999).
[2] Z. Wang, Z. Q. Chen, J. Zhu, S. J. Wang, and X. Guo, Radiat. Phys. Chem. **58**, 697 (2000).
[3] J. E. Garay, S. C. Glade, P. Asoka-Kumar, and U. Anselmi-Tamburini, J. Appl. Phys. **99**, 024313 (2006).
[4] Y. Yagi, S. Hirano, Y. Ujihira, and M. Miyayama, J. Mater. Sci. Lett. **18**, 205 (1999).
[5] O. Melikhova, J. Kuriplach, J. Cizek, I. Prochazka, W. Anwand, G. Brauer, T. E. Konstantinova, and I. A. Danilenko, phys. stat. sol. (c) **4**(10), DOI 10.1002/pssc.200775858 (2007). (this issue).
[6] T. Konstantinova, I. Danilenko, N. Pilipenko, and A. Dobrikov, in: 9th Cimtec – World Ceramics Congress. Ceramics: Getting into the 2000's – Part A, edited by P. Vincenzini, Techna Srl. 1999, p. 305. A. M. Slipenyuk, M. D. Glinchuk, I. P. Bykov, A. V. Ragulya, V. P. Klimenko, T. E. Konstantinova, and I. A. Danilenko, Ferroelectrics **298**, 289 (2004).
[7] F. Becvar, J. Cizek, L. Lestak, I. Novotny, I. Prochazka, and F. Sebesta, Nucl. Instrum. Methods A **443**, 557 (2000).
[8] J. Cizek, F. Becvar, I. Prochazka, and J. Kocik, Mater. Sci. Forum **445/446**, 63 (2004).
[9] K. Ito, H. Nakanishi, and Y. Ujihira, J. Phys. Chem. B **103**, 4555 (1999).