

Positron-annihilation and photoluminescence studies of nanostructured ZrO₂

Janusz D. Fidelus,
Andrzej Karbowski,
Sebastiano Mariazzi,
Roberto S. Brusa,
Grzegorz Karwasz

Abstract. In the present work, photoluminescence and Doppler broadening depth-resolved positron annihilation spectroscopy was performed on pure zirconia nanopowders. Zirconia nanopowders were grown by a hydrothermal microwave-driven process followed by annealing in oxygen atmosphere. Photoluminescence under 274 nm wavelength excitation from a 150 W high-pressure Xe exhibits similar spectra, in the region from 320 to 820 nm, although its intensity depends on the annealing. Positron annihilation Doppler-broadening spectra show low values of the normalized S -parameter, varying little with the depth, from 0.495 on the surface to 0.47–0.49 in bulk. Both high the annealing temperature and oxygen concentrations, lead to low bulk S -values. The *ortho*-positronium (*o*-Ps) fraction is about 10–11% for all samples on the surface, whereas it is reduced to 7–8% in the bulk for samples annealed at 700°C and 5–6% for samples annealed at 800°C. Both photoluminescence (PL) and positron studies show the presence of defects in all samples. The *o*-Ps signal suggests a high porosity of samples, particularly at a depth down to 10 nm.

Key words: positron annihilation • zirconia nanopowders • photoluminescence

J. D. Fidelus
Institute of High Pressures of the Polish Academy
of Sciences,
29/37 Sokołowska Str., 01-142 Warsaw, Poland

A. Karbowski[✉], G. Karwasz
Institute of Physics,
Nicolaus Copernicus University (UMK),
5 Grudziądzka Str., 87-100 Toruń, Poland,
Tel.: +48 56 611 3291, Fax: +48 56 622 5397,
E-mail: akarb@fizyka.umk.pl

S. Mariazzi, R. S. Brusa
Dipartimento di Fisica,
Università di Trento,
14 Sommarive Str., I-38100 Povo (Trento), Italy

Received: 8 June 2009
Accepted: 5 October 2009

Introduction

Zirconia (ZrO₂) ceramics has interesting mechanical and ionic properties which make it possible its use as structural and wear components, oxygen gas sensors. It is also used in solid oxide fuel cells due to its high oxygen ion conductivity. It is used as a grinding medium and engineering ceramics, due to its high hardness and high thermal shock resistivity. Therefore, the material properties, including optical properties, are of a high interest. For zirconia luminescent phosphors, a recent observation shows a huge sensitizing of lanthanides by Y₂O₃ co-doping [7, 8].

Usually, zirconia is stabilized by adding a few percent of Y₂O₃ which prevents the phase transformation of zirconia (occurring at about 1170°C) from a monoclinic to the tetragonal form (what is accompanied by a large volume shrinkage). Previous studies of zirconia, both with photoluminescence [7, 8, 15, 16, 20] and positron annihilation [4, 9, 10, 12, 17] techniques were performed mostly for fully stabilized ZrO₂:Y samples. The luminescence intensity of ZrO₂ nanocrystals depends on the temperature during heating and cooling in vacuum [14]. The luminescence of nanocrystalline ZrO₂ annealed in oxygen and nitrogen mixtures depends also on the oxygen partial pressure [6, 18]. The properly produced ZrO₂ luminescent powder is very promising as a material for oxygen detector [5, 6, 18, 19].

Our previous studies [20] of tetragonal ZrO₂:Y nanopowders under 266 nm laser excitation showed a broad photoluminescence band extending from 350 to 700 nm and centered at a 500 nm wavelength. A similar band, slightly narrowed and shifted to longer (550 nm) wavelength was observed in the same study for a tetragonal ZrO₂:Y single crystal sample [20].

Positron annihilation spectroscopy (PAS) [3, 11] is a powerful tool in analyzing defects in semiconductors, glasses, porous materials, etc. Apart from the recent work by Garay *et al.* [9], who used Doppler-broadening coincidence techniques, the majority of previous studies [4, 10, 12, 17] yielded positron lifetimes in ZrO₂:Y.

Experimental

Samples were prepared from zirconia nanopowders grown by a hydrothermal microwave-driven process. The precursor solution was zirconium (IV) oxide chloride octahydrate (ZrOCl₂ × 8H₂O) 99.5% purity (Riedel-de Haen) in distilled water, with pH of 10 adjusted by adding 1 M NaOH. The synthesis time was 30 min (20 min heating, 10 min cooling), at a 6 MPa pressure in a microwave ERTEC reactor (Wrocław) and at 280°C. The precipitates obtained were filtered, washed with distilled water, dried at 90°C for 24 h and ground. The powders obtained were annealed subsequently at 700°C and 800°C at a rate of 15°C/min and then held at the same temperature for 30 min. The reason for this latter treatment was to obtain a proper crystalline phase and the grain size. Details of microwave hydrothermal processing are described elsewhere [5]. Pellets of 1 cm in diameter and 1 mm in thickness were formed under a 130 MPa pressure.

The temperature of 700°C was found to be optimal from the point of view of the grain size and the crystal structure which, after cooling, remains a mixture of tetragonal and monoclinic phases. The thermal treatment at 800°C was applied in order to get monoclinic ZrO₂ nanopowder. Physical properties of obtained nanostructured samples, exhibiting the grain size of 23 to 33 nm, and surface area of 36 to 12 m²/g after annealing at 700–800°C temperature, respectively, differ from those of bulk ZrO₂.

The two series of samples (treated at 700°C and 800°C) were subsequently annealed for 20 min in an oxygen-nitrogen atmosphere (1 atm pressure) with different O₂ content (2.6%, 14.8%, 21%) or in vacuum (10⁻⁴ mbar) at 340°C.

Photoluminescence studies were performed at room temperature using a SM2203 spectrofluorimeter with two double built-in monochromators. The 150 W high-pressure Xe lamp was used as the excitation source, and a R-928 Hamamatsu photomultiplier for PL detection.

Present positron measurements were done by Doppler broadening PAS (DB-PAS) technique at the Trento laboratory [2, 21]. The measurements were carried out with an electrostatic slow positron beam tunable in the 0.05–25 keV energy range which corresponds to a depth scale of 1 to about 1000 nm. The mean positron implantation depth z is related to the positron implantation energy E through the equation:

$$(1) \quad Z = (40/\rho)E^{1.6}$$

where Z is in nanometers; ρ – density is expressed in grams per cubic centimeter and energy E in keV, respectively [1]. The ZrO₂ density of 5.6 g/cm³ was used for the calculation of the positron implantation depth; this actually can lead to an underestimation of the implantation depth as the real density of present nanostructured pellets is somewhat lower (within 5% [5]). 511 keV gamma detection was performed by a high-purity Ge detector (resolution of 1.2 keV at 511 keV with a 6 μ s shaping time). The spectra were characterized by the shape parameter S , defined as the ratio of the counts in a central area ($|511 - E_\gamma| \leq 0.85$ keV) of the annihilation line and the total area ($|511 - E_\gamma| \leq 4.25$ keV) and the wing parameter W defined as the fraction of the counts in the wing region ($1.6 \leq |E_\gamma - 511| \leq 4$ keV) of the peak. The S parameter represents the fractions of positrons annihilating with low momentum electrons, while the W parameter represents the fraction of positrons annihilating with high momentum electrons (outermost core electrons); more than 2.5×10^5 counts in each annihilation spectrum were recorded.

Three-gamma annihilation signal indicates the formation of positronium atom inside the material, or in other words, the presence of large open volumes (comparable with atomic radii). The $2-3\gamma$ ratio was calculated as the ratio between the valley area (E_γ between 410–500 keV) and the 511 keV peak area ($|511 - E_\gamma| \leq 4.25$ keV) [$R(E)$ parameter]. The $R(E)$ parameter was calibrated by measuring the Ps formation in a Ge crystal (111) as a function of the temperature. The Rn (%) calibrated parameter is defined as $(R - R_0)/(R_\infty - R_0)$. It is assumed R_∞ (100% positronium formation), the R value being obtained by extrapolating to zero implantation energy R measured in Ge at 1000 K. At this temperature, all positrons at the surface form positronium. As R_0 (0% positronium formation), the R value at the highest positron implantation energy was assumed. Positrons do not form Ps in the Ge bulk. In our measurements we obtain directly the percentage of the *o*-Ps fraction ($R\%$) in the total annihilation signal, by normalization of the three-gamma signal to that from germanium samples at 800°C [13] where we assume $R = 100\%$.

Results and discussion

Positron annihilation S -parameter dependences on the incident positron energy (i.e. on the implantation depth) are shown in Fig. 1 for samples sintered at 700°C and in Fig. 2 for samples sintered at 800°C. For all samples, the S -parameter varies little with the positron implantation energy, indicating that samples are rather homogenous in depth. Some rise of the S -parameter on the surface is probably related to the formation of the positronium atom. The single series in Figs. 1 and 2 show, apparently, little difference but the general tendency is clear: the rise of the treating temperature and the oxygen content in the annealing phase reduces the S -parameter indicating less defects.

In all samples the three-gamma annihilation signal is high and rises towards the surface, for the 10 nm depth, see Figs. 3 and 4. This indicates the presence of relatively large free volumes (of the order of few atomic units, at least) in the near-to-surface layer. Note that

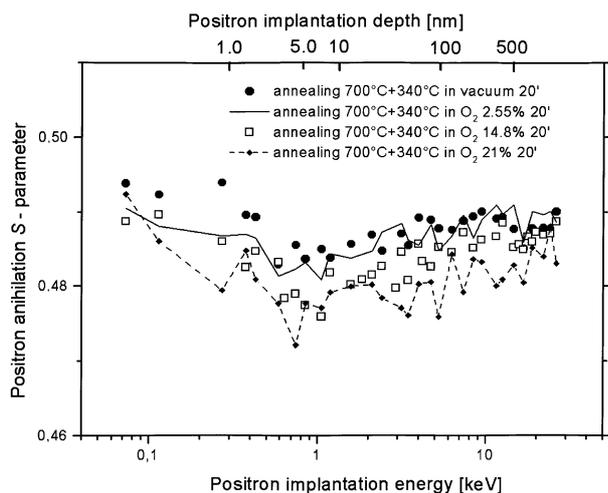


Fig. 1. Positron annihilation Doppler broadening S – parameter for nanostructured pure zirconia samples, treated at 700°C and annealed in oxygen-nitrogen atmosphere with different O₂ content.

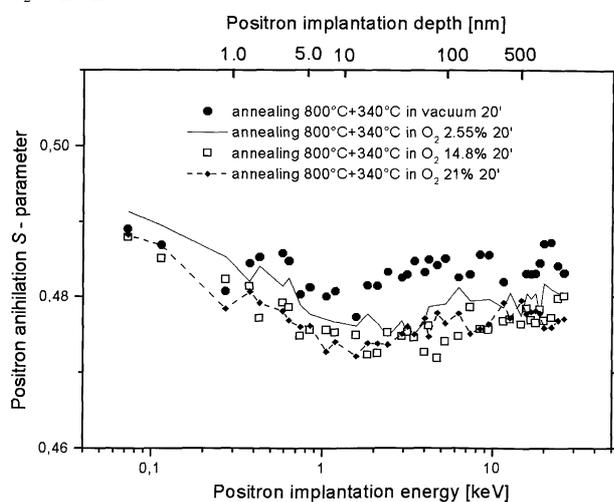


Fig. 2. Positron annihilation Doppler broadening S – parameter for nanostructured pure zirconia samples, treated at 800°C and annealed in oxygen-nitrogen atmosphere with different O₂ content.

such a feature is particularly important in gas-sensor applications. The samples treated at 700°C (tetragonal and monoclinic phases), and in particular annealed with higher oxygen content show a relatively higher positronium fraction in the bulk. Note, however, that the o -Ps signal depends not only on the open volumes but also on the surface features (chemical terminations) of the nanograins. In fact, annealing of 700°C samples at low-oxygen contents (2.6%) even rises the o -Ps signal, see Fig. 3. Probably, terminating the surface with oxygen atoms facilitates o -Ps formation.

Presence of large open volumes was observed also in positron lifetime measurements of pressed (250 MPa) nanostructured pure zirconia pellets [17]. In those measurements apart from short lifetime components (189 ps and 373 ps) attributed in Ref. [17] to annihilation inside nanograins and on the grain boundaries, respectively, two long lifetime components (2 and 34 ns, with 1.5% and 7.4% intensities, respectively) were observed. In particular, this latter lifetime is to be related to large open volumes between grains. Also the shortest component can be attributed to free $para$ -positronium (p -Ps) annihi-

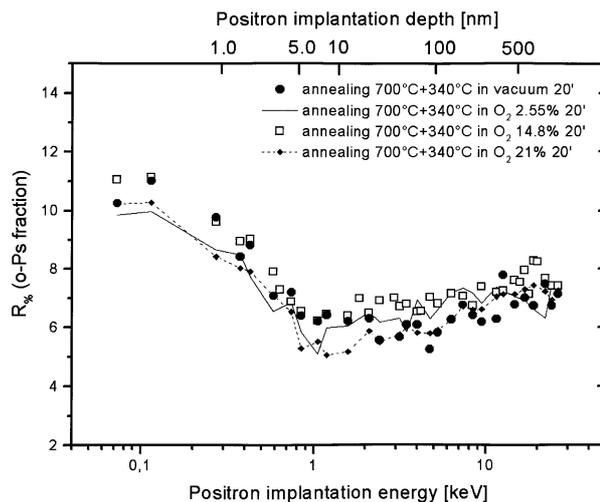


Fig. 3. Fraction of o -Ps annihilation in nanostructured pure zirconia samples, treated at 700°C and annealed in oxygen-nitrogen atmosphere with different O₂ contents.

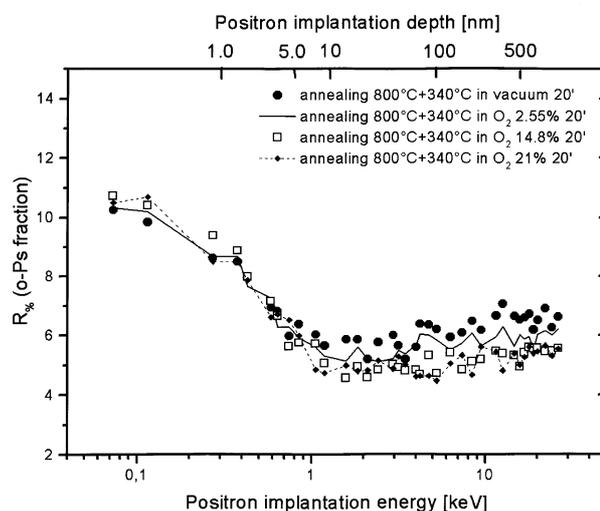


Fig. 4. Fraction of o -Ps annihilation in nanostructured pure zirconia samples, treated at 800°C and annealed in oxygen-nitrogen atmosphere with different O₂ content.

lation. Long-life components disappear after sintering at 1200°C [17]. Note, however, that for getting fully compact zirconia ceramics usually applied sintering temperature is 1100–1300°C [17].

Photoluminescence spectra are shown in Fig. 5 for samples treated at 700°C and in Fig. 6 for samples treated at 800°C. All spectra are broad, extending from about 350 to 700 nm wavelength (from about 1.8 to 3.5 eV emitted photon energy) and peak at about 3.0 eV photon energy (420 nm). The intensity of the PL for samples annealed in vacuum is lower by a factor of 2 for pellets formed at 800°C as compared to pellets formed at 700°C compare Figs. 5 and 6 (note different PL intensity scales).

Annealing in oxygen atmosphere reduces the PL signal in all samples. For samples treated at 700°C, the oxygen content must be higher (14.8%) in order to obtain the same quenching of the PL signal as that in samples treated at 800°C and annealed with lower oxygen content (2.6%).

Some shoulder is observed at about 600 nm on both figures for samples annealed in the vacuum; the inten-

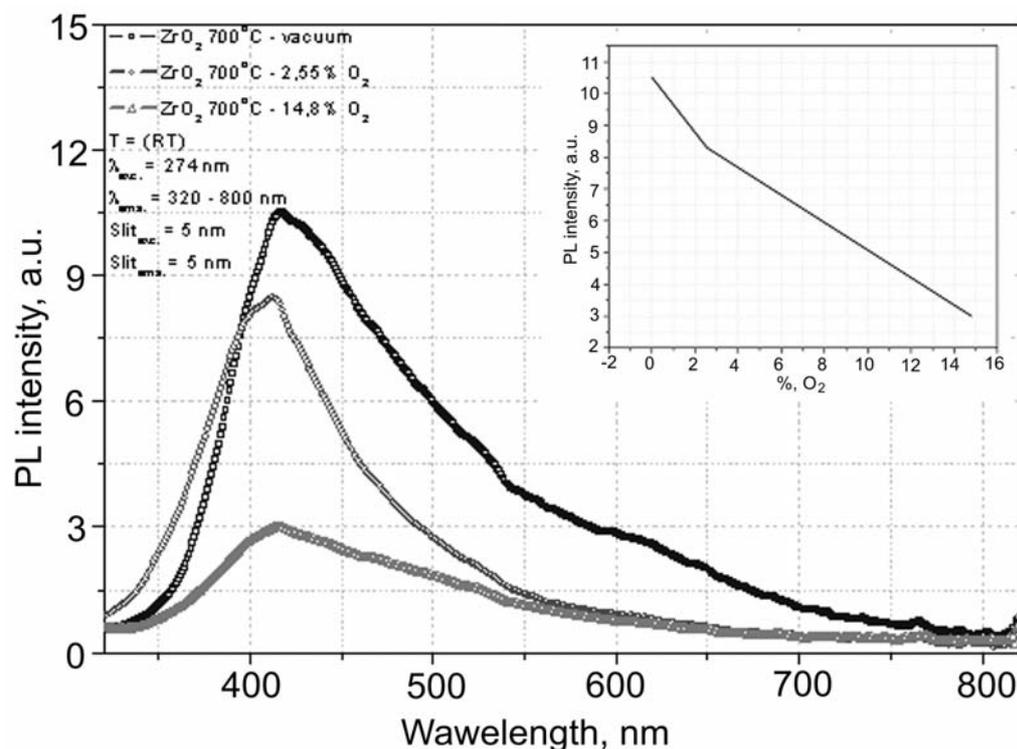


Fig. 5. Luminescence intensity for nanostructured ZrO_2 treated at 700°C and annealed at 340°C (20 min) in different oxygen content (0%, 2.55%, 14.8%) with nitrogen being the remaining atmosphere component. The inserts document the PL intensity dependence on oxygen pressure. Excitation at 274 nm at room temperature (RT).

sity of this shoulder does not change with the rise of the annealing temperature. Yellow-orange PL was observed in tetragonal and cubic polycrystalline $\text{ZrO}_2\text{:Y}$ and attributed to some structure disorder [15]. In the previous studies [20] of single crystal $\text{ZrO}_2\text{:Y}$, a similar, side-band peak in the photoluminescence signal was observed.

Since the band gap of tetragonal ZrO_2 is above 5 eV the observed broad PL bands are tentatively attributed to some defects in the material. Quenching of the PL bands, particularly visible after treating at 800°C , for even small oxygen concentrations, indicate that these are zirconium-oxygen ZrO_{2-x} non-stoichiometric

complexes responsible for the PL signal. However, probably at least two different centers are involved in the photoluminescence. The main peak in PL is significantly reduced in samples treated at 800°C (and with no oxygen atmosphere annealing) as compared to 700°C what suggests the role of defects or low dimensional structures, like grain borders in PL. The latter observation is congruent with PAS studies. In fact, S -parameter values for the samples annealed at 700°C and subsequently in 14.8% oxygen atmosphere coincide within the experimental uncertainty with the values for the sample annealed at 800°C in vacuum.

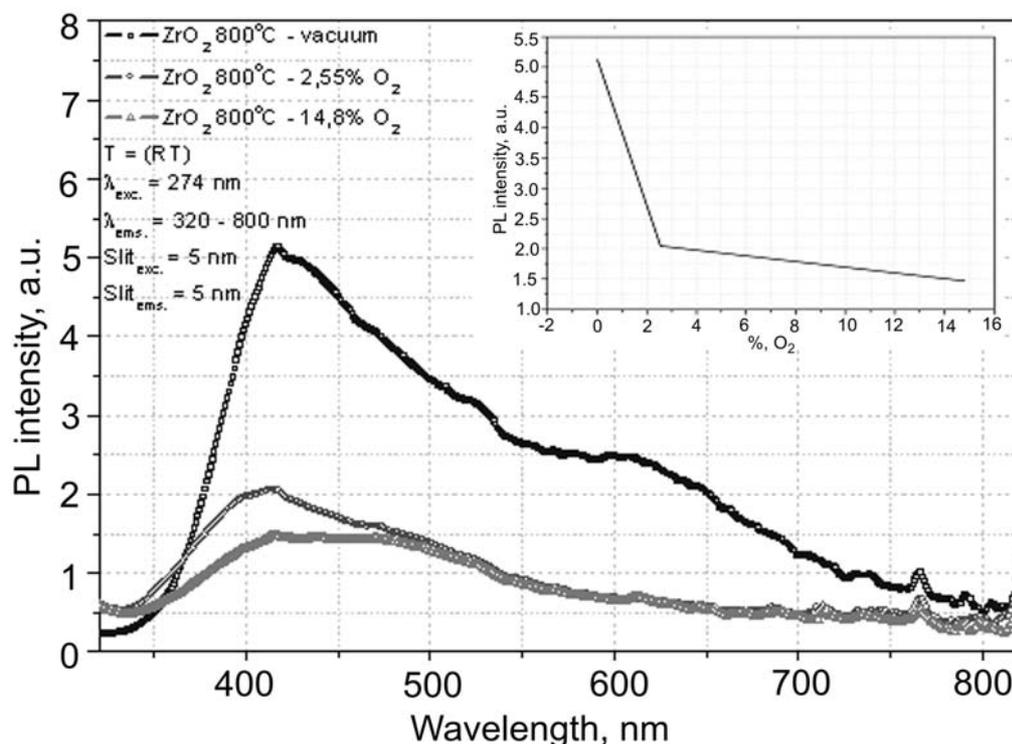


Fig. 6. Luminescence intensity for nanostructured ZrO_2 treated at 800°C and annealed at 340°C (20 min) in different oxygen content (0%, 2.55%, 14.8%) with nitrogen being the remaining atmosphere component. The inserts document the PL intensity dependence on oxygen pressure. Excitation at 274 nm at RT.

In the previous studies [20] for ZrO₂:Y a shift of the PL peak position with the excitation photon energy was noticed. That shift suggested that the zirconium-oxygen complexes are distorted with the distortion depending on the distance to the intrinsic defect (e.g. oxygen vacancy) [20]. The present measurements confirm this hypothesis.

Conclusions

Photoluminescence and positron annihilation studies were performed on pure zirconia nanostructured samples. Observed broad PL bands indicate Zr-O complexes related to some defects as the PL source. Positron studies indicate the presence of large free volumes, open towards the sample surface. Treating at 800°C, and annealing in the oxygen atmosphere reduces significantly the PL signal. A reduction of the defect contents is visible also in lowering the positron annihilation *S*-parameter. In order to identify the nature of the PL (and defect) centers, the site-sensitive PAS measurements (Doppler-coincidence) are planned. Additionally, measurements on samples with higher sintering temperatures would be useful in order to identify the limit for the presence of large open volumes, as seen by PAS.

Results of these investigations may contribute to explaining how the excess from ZrO₂ stoichiometry influences the luminescence properties of this material. Understanding of this phenomenon is likely to be meaningful for studies of related processes occurring in other binary oxides such as ZnO and TiO₂ etc.

Acknowledgment. This work was partially supported by grant no. N N508 0851 33 of the Ministry of Science and Higher Education (Poland) donated for the years 2007–2009 and by UMK Rector, grant no. 524-F. One of the authors (JDF) thanks Sergey Yatsunenko for his assistance with the PL measurements. We thank the referee for noting the inconsistency in the lifetime interpretation in Ref. [17].

References

- Asoka-Kumar P, Lynn GK, Welch DO (1994) Characterization of defects in Si and SiO₂-Si using positrons. *J Appl Phys* 76 9:4935–4982
- Brusa RS, Karwasz GP, Bettonte M, Zecca A (1997) High performance electrostatic positron beam. *Appl Surf Sci* 116:59–62
- Brusa RS, Macchi C, Mariazzi S, Karwasz GP, Scarel G, Fanciulli M (2007) Innovative dielectrics for semiconductor technology. *Rad Phys Chem* 76:189–195
- Chakrabarti M, Bhowmick D, Sarkar A *et al.* (2005) Doppler broadening measurements of the electron-positron annihilation radiation in nanocrystalline ZrO₂. *J Mater Sci* 40:5265–5268
- Fidelus JD, Łojkowski W, Millers D, Grigorjeva L, Smits K, Piticescu RR (2007) Zirconia based nanomaterials for oxygen sensors – generation, characterisation and optical properties. *Solid State Phenom* 128:141–150
- Fidelus JD, Millers D, Łojkowski W, Grigorjeva L, Smits K (2006) Zirconia based nanomaterials for luminescent oxygen sensors. In: *Proc of the 9th Scientific Conf Optoelectronic and Electronic Sensors (COE 2006)*, 19–22 June 2006, Kraków–Zakopane. AGH, Kraków, pp 307–310
- Fidelus JD, Yatsunenko S, Godlewski M, Łojkowski W, Paszkowicz W, Werner-Malento E, Chudoba T, Opalińska A (2009) Relation between structural properties of Pr³⁺-doped yttria-stabilized zirconia nanopowders and their luminescence efficiency. Patent application P-387855 (in Polish)
- Fidelus JD, Yatsunenko S, Godlewski M, Paszkowicz W, Werner-Malento E, Łojkowski W (2009) Relation between structural properties of Pr³⁺-doped yttria-stabilized zirconia nanopowders and their luminescence efficiency. *Scripta Mater* 61:415–418
- Garay JE, Glade SC, Asoka-Kumar P, Anselmi-Tamburini U, Munir ZA (2006) Characterization of densified fully stabilized nanometric zirconia by positron annihilation spectroscopy. *J Appl Phys* 99:024313
- Guo X, Wang Z (1998) Effect of niobia on the defect structure of yttria-stabilized zirconia. *J Eur Ceramic Soc* 18:237–240
- Karwasz GP, Zecca A, Brusa RS, Pliszka D (2004) Application of positron annihilation techniques for semiconductor studies. *J Alloys Compd* 382:244–251
- Lai LJ, Su Ch (2000) Luminescence excitation and near edge X-ray absorption spectra of Er₂O₃ dopant on zirconia ceramics. *Mater Chem Phys* 62:148–152
- Mariazzi S, Patel N, Toniutti L, Checchetto R, Miotello A, Brusa RS (2007) Structural characterization and porosity analysis in spin coated silica thin films as gas selective membranes. *Phys Status Solidi C* 4:3823–3826
- Millers D, Grigorjeva L, Opalińska A, Łojkowski W (2003) Luminescence of nanosized ZrO₂ and ZrO₂:Pr powders. *Solid State Phenom* 94:135–140
- Paje SE, Lopis JL (1996) Disorder effects on the luminescence decay in yttria-stabilized zirconia polycrystals. *J Phys D: Appl Phys* 29:442–445
- Petrik NG, Taylor DP, Orlando TM (1999) Laser-stimulated luminescence of yttria-stabilized cubic zirconia crystals. *J Appl Phys* 85:6770–6776
- Procházka I, Čížek J, Kuriplach J, Melikhova O, Konstantinova TE, Danilenko IA (2008) Positron lifetimes in zirconia-based nanomaterials. *Acta Phys Pol A* 113;5:1495–1499
- Smits K, Grigorjeva L, Łojkowski W, Fidelus JD (2007) Luminescence of oxygen related defects in zirconia nanocrystals. *Phys Status Solidi C* 4;3:770–773
- Smits K, Grigorjeva L, Millers D, Fidelus JD, Łojkowski W (2008) Radiative decay of electronic excitations in ZrO₂ nanocrystals and macroscopic single crystals. *IEEE Transaction Nucl Sci* 55;3:1523–1526
- Smits K, Millers D, Grigorjeva L, Fidelus JD, Łojkowski W (2007) Comparison of ZrO₂:Y nanocrystals and macroscopic single crystal luminescence. *J Phys: Conf Series* 93:012035
- Zecca A, Bettonte M, Paridaens J, Karwasz GP, Brusa RS (1998) A new electrostatic positron beam for surface studies. *Meas Sci Technol* 9:409–416