Characterization of point defects in yttria stabilized zirconia single crystals

O Melikhova¹, J Cizek¹, J Kuriplach¹, I Prochazka¹, W Anwand², G Brauer² and D Grambole³

¹ Charles University in Prague, Faculty of Mathematics and Physics, V Holesovickach 2, CZ-18000 Prague 8, Czech Republic
² Institut für Strahlenphysik, Forschungszentrum Dresden-Rossendorf, PO Box 510119, D-01314 Germany
³ Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Dresden-Rossendorf, PO Box 510119, D-01314 Germany

E-mail: oksivmel@yahoo.com

Abstract. Characterization of point defects in a fully stabilized ZrO₂ + 9 mol.% Y₂O₃ single crystal with cubic structure was performed in this work. It was found that the crystal contains a high density of vacancy-like defects characterized by a lifetime of 175 ps. First principle theoretical calculations showed that this lifetime is comparable with lifetime of positrons trapped in zirconium vacancies associated with hydrogen. In particular, in the vicinity of the zirconium vacancy hydrogen forms an O-H bond with one of the nearest neighbour oxygen atoms. The calculated bond length is close to 1 Å. Using nuclear reaction analysis it was found that the hydrogen concentration in the crystal is 0.3 at.%. This amount of hydrogen is sufficient to form zirconium vacancy – hydrogen complexes capable of saturated positron trapping.

1. Introduction
Zirconia (ZrO₂) exhibits a high thermal stability and a low thermal conductivity together with good mechanical properties [1]. At temperatures above 1380 °C zirconia exists in a high temperature cubic phase, which transforms into a tetragonal one and subsequently into a monoclinic phase at lower temperatures. The high temperature cubic phase can be stabilized down to room temperature by addition more than 8 mol % of trivalent yttria (Y₂O₃) [2]. Such a system is then called yttria stabilized zirconia (YSZ). An embedment of Y₂O₃ into the ZrO₂ host lattice leads to a deviation from stoichiometry resulting in the creation of a high amount of native oxygen vacancies (V₀). Hence, vacancies play certainly a very important role in YSZ.

The purpose of this work is the characterization of vacancies in a high quality YSZ single crystal employing positron lifetime (LT) measurements and slow positron implantation spectroscopy (SPIS). In order to facilitate interpretation of experimental data, we performed also theoretical modeling of defects in YSZ by state-of-the-art ab initio electronic structure calculations including ionic relaxations.

2. Experimental
ZrO₂ + 9 mol.% Y₂O₃ single crystal with (100) orientation and dimensions 10 × 10 × 0.5 mm³ was grown by skull melting method and supplied by Crystec GmbH, Berlin. Surface of the crystal was
optically polished. A digital LT spectrometer [3] with an excellent time resolution of 145 ps (FWHM 22Na) was employed for LT measurements. SPIS investigations were performed on the magnetically guided variable energy slow positron beam SPONSOR [4]. The energy of incident positrons can be varied in the range from 0.03 to 36 keV. Doppler broadening of annihilation profile was analyzed using the $S$ parameter. The hydrogen concentration in the crystal was determined by nuclear reaction analysis (NRA) using the resonant nuclear reaction $^{15}$N + $^1$H → $^{12}$C + $^4$He + $\gamma$ rays. The hydrogen concentration was determined at a sample depth of ~ 100 nm using $^{15}$N ions accelerated to 6.64 MeV.

| positron state | $\tau$ (ps) | $E_B$ (eV) |
|---------------|-------------|-------------|
| Bulk          | 151         | -           |
| $V_O$         | 153         | 0.05        |
| $V_{Zr}$      | 287         | 2.33        |
| $V_{Zr} + H$  | 175         | 1.83        |
| $V_{Zr} + 2H$ | 172         | 0.88        |
| $V_{Zr} + 4H$ | 155         | 0.08        |
| $V_{Zr} + 6H$ | 150         | 0.00        |

Table 1. Results of ab-initio theoretical calculations of positron parameters: bulk positron lifetime for ZrO$_2$ crystal, positron lifetimes $\tau$ and binding energies $E_B$ for various defects including O-vacancy ($V_O$), Zr-vacancy ($V_{Zr}$) and Zr vacancy associated with various number of hydrogen atoms ($V_{Zr} + nH$).

3. Theoretical calculations

*Ab initio* calculations of atomic relaxations around defects were determined using the Vienna *ab initio* simulation package (VASP) [5] employing a generalized gradient approximation (GGA) projector augmented-wave (PAW) pseudopotential. 4s, 4p, 5s and 4d Zr electrons and 2s and 2p O and 1s H electrons were included in the self-consistent calculations of electronic structure and ion relaxations. Defects were modeled in the cubic ZrO$_2$ (fluorite) lattice with the lattice parameter $a = 5.08$ Å [6] using 96 atom-based supercells employing $2\times2\times2 k$-mesh sampling centered at the $\Gamma$ point.

Positron lifetimes and positron binding energies to defects were calculated in the limit of vanishing positron density [7]. The self-consistent valence electron density calculated by VASP with added frozen core electrons was used in positron calculations. Hence charge transfer is included in the calculations of positron parameters. Since in our previous calculations [8] we found that the GGA scheme for electron-positron correlations formulated by Barbiellini et al. [9] when used with self-consistent electron density gives positron lifetimes which are in the best agreement with experiment, we used this scheme in all calculations in this paper.

4. Results and discussion

LT measurements revealed that the YSZ crystal exhibits a single component spectrum (apart from the source component) with a lifetime of $(175 \pm 1)$ ps, which is remarkably longer than the calculated bulk lifetime in zirconia (see table 1). This testifies that YSZ crystal contains a high density of defects which cause saturated positron trapping. This is also supported also by SPIS results: the dependence of the $S$ parameter on the positron energy is plotted in figure 1. The solid line in the figure is a model
function calculated by the VEPFIT software [10] assuming a single layer model. A very short positron diffusion length $L_+= (8.6 \pm 0.4)$ nm obtained from fitting gives a strong evidence that almost all positrons are trapped at defects. The concentration of defects can be estimated from SPIS results using the relation

\[ c = \frac{1}{\nu \tau_B} \left( \frac{L_{B,+}^2}{L_{+}^2} - 1 \right), \]

where $\tau_B$ and $L_{B,+}$ denote, respectively, the bulk positron lifetime and diffusion length in a perfect ZrO$_2$ lattice, while $L_+$ is the mean positron diffusion length measured in the sample. Here we used the calculated zirconia bulk lifetime $\tau_B = 151$ ps (see table 1) and $L_{B,+} \approx 150$ nm, which is a typical positron diffusion length in similar materials [7]. Using the specific trapping rate $\nu \approx 10^{14}$ at. s$^{-1}$, which is a typical value for monovacancies in most solids [7], equation (1) gives the defect concentration in YSZ crystal $c \approx 2$ at.%. Despite of uncertainties of input quantities, it is clear that the YSZ crystal studied exhibits a very high concentration of defects comparable in order of magnitude with the concentration of substitutional Y atoms (6.2 at.%).

Figure 2. Relaxed geometries for VZr associated with various number of hydrogen atoms (VZr + nH). Relaxed positions of the nearest neighbour O atoms and trapped H atoms are shown by filled symbols, while open symbols show positions in the rigid lattice. The values in the figure are displacement magnitudes (in Å) and directions. Displacements of H atoms are given with respect to the site in the middle of a line connecting the vacancy and the nearest neighbour O atom.

Table 1 shows calculated positron lifetimes for a perfect ZrO$_2$ crystal and various defect configurations. Our previous calculations [8,11] showed that VO and also its complexes with Y atoms are too shallow traps unable to confine positrons. Hence positron traps detected in the YSZ crystal should be defects containing the zirconium vacancy (VZr), which is a deep positron trap [8,11].

However, one can see in the table 1 that calculated lifetime of positrons trapped in VZr is longer than 175 ps determined in experiment. Note that Damonte et al. [12] found in ZrO$_2$ + 8 mol.% Y$_2$O$_3$ crystal a component with lifetime of 196 ps, i.e. again shorter lifetime than that calculated for VZr. A shortening of the positron lifetime may be caused by some impurity associated with VZr, which reduces its free volume. When considering possible impurities, hydrogen is the most promising candidate. First, the presence of hydrogen can hardly be avoided in any method of crystal growth. Second, hydrogen is usually highly mobile in materials and can be relatively easily incorporated into the ZrO$_2$ structure due its tendency to bind with oxygen.
Indeed, nuclear reaction analysis (NRA) shows that the hydrogen concentration in the studied single crystal is \((0.33 \pm 0.03)\) at.\% and hydrogen is in a ‘tightly bound’ state in the lattice. Although the hydrogen concentration determined by NRA is lower than the estimated concentration of \(V_{Zr}\), it is still high enough to cause saturated positron trapping in \(V_{Zr} + nH\) complexes.

Figure 2 shows relaxed geometries of \(V_{Zr}\) complexes with hydrogen considered in this work. In general our calculations indicate that hydrogen is trapped in \(V_{Zr}\) and forms an O-H pair with one of the nearest neighbor O atoms. In case of multiple H atoms trapped in \(V_{Zr}\), multiple O-H pairs are formed. Trapped H atoms are always displaced towards one of the nearest neighbor O anion, which relaxes slightly toward hydrogen. In \(V_{Zr} + 1H\) and \(V_{Zr} + 2H\) complexes H relaxes outward in the <111> direction, while O relaxes inward. The O anions which did not form O-H pairs relax outward. If more H atoms are trapped in \(V_{Zr}\), then their mutual repulsion leads to displacements in a direction other than <111>. However, one can always observe the coupling of H and O atoms and formation of an O-H pair with bond length close to 1 Å.

Hydrogen associated with \(V_{Zr}\) causes a reduction of free volume and an increase of local electron density in vacancy. This is reflected by a remarkable shortening of the positron lifetime which can be seen in table 1. Note that \(V_{Zr}\) associated with more than 4 H atoms is not capable of positron trapping anymore. For this reason we stopped our calculations at \(V_{Zr} + 6H\) complex. The calculated lifetime of positrons trapped in \(V_{Zr} + 1H\) and \(V_{Zr} + 2H\) agree well with the lifetime measured on the YSZ crystal. Hence, our calculations suggest that YSZ crystal contains \(V_{Zr}\) associated with hydrogen.

5. Conclusions
Characterization of point defects in \(ZrO_2 + 9\) mol.\% \(Y_2O_3\) single crystal was performed in this work. The crystal contains high density of defects related to \(V_{Zr}\). First principles calculations indicate that \(V_{Zr}\) may be associated with hydrogen introduced into the sample unintentionally during the growing process. Nuclear reaction analysis revealed that the crystal indeed contains noticeable amount of hydrogen. Hence, hydrogen should be seriously considered as an important impurity in YSZ crystals.

Acknowledgments
This work was supported by the Academy of Science of the Czech Republic (project KJB101120906) and the Ministry of Schools, Youths and Sports of the Czech Republic (projects MSM 0021620834 and COST OC 165).

References
[1] Ryschkewitz E and Richardson D W 1985 Oxide Ceramics: Physical Chemistry and Technology (Hasskel, General Ceramics)
[2] Goff J P, Hayes W, Hull S, Hutchings M T and Clausen K N 1999 Phys. Rev. B 59 14202
[3] Becvar F, Cizek J, Prochazka I 2008 Appl. Surf. Sci. 255 111
[4] Anwand W, Kissener H-R and Brauer G 1995 Acta Phys. Polon. A 88 7
[5] Kresse G and Hafner J 1994 Phys. Rev. B 49 14251
[6] Howard C J, Hill R J and Reichert B E 1988 Acta Crystallogr. Sect. B: Struct. Sci. 44 116
[7] Puska M J and Nieminen R M 1994 Rev. Mod. Phys. 66 841
[8] Melikhova O, Kuriplach J, Cizek J, Prochazka I, Brauer G, Anwand W 2010 J. Phys.: Conf. Series 225 012035
[9] Barbiellini B, Puska M J, Korhonen T, Harju A, Torsti T and Nieminen R M 1996 Phys. Rev. B 53 16201
[10] van Veen A, Schut H, Clement M, de Nijs J, Kruseman A and Ijpma M 1995 Appl. Surf. Sci. 85 216
[11] Cizek J, Melikhova O, Prochazka I, Kuriplach J, Kuzel R, Brauer G, Anwand W, Konstantinova T E and Danilenko I A 2010 Phys. Rev. B 81 024116
[12] Damonte LC, Taylor MA, Desimoni J, Runco J 2007 Rad. Phys. Chem. 76 248