Defect studies of zirconia implanted by high energy Xe ions

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Abstract. In the present work positron lifetime spectroscopy was employed for characterization of radiation-induced defects in yttria stabilized zirconia (YSZ) implanted by 167 MeV Xe ions. Positron lifetime data were interpreted with aid of ab-initio theoretical modelling of defects in YSZ lattice. Damage caused by Xe implantation was investigated in two YSZ samples with different microstructure: (i) single crystal and (ii) sintered ceramic. The virgin YSZ single crystal exhibits single component spectrum with lifetime of ≈ 180 ps. Similar lifetime component was found also in the virgin sample of sintered YSZ ceramic. Since this lifetime is significantly higher than the YSZ bulk lifetime the virgin YSZ crystal and the sintered ceramic both contain vacancy-like defects. Xe implantation leads to appearance of additional defect component with longer lifetime ≈ 370 ps which comes obviously from vacancy clusters formed by agglomeration of irradiation induced vacancies. A broad absorption band with peak absorption at ≈ 518 nm was found in Xe-implanted crystal by optical measurements.

1. Introduction

Zirconia (ZrO₂) is used in a wide range of high temperature applications due to its high melting point, low thermal conductivity, high strength and good fracture toughness [1]. Moreover, zirconia is known as radiation hard material resistant against radiation damage [2]. However, the pure zirconia, which is monoclinic at room temperature, undergoes a transformation to the tetragonal phase at 1100°C temperature. Such a transformation is connected with a considerable volume shrinkage leading even to a creation of cracks within ZrO₂ structure [3]. Obviously, this effect inhibits any use of the pure zirconia in high temperature applications. Thus, a stabilization of the high-temperature ZrO₂ phase is required to make a full use of advantageous zirconia features in industry. This can be achieved by an addition of trivalent yttrium oxide Y₂O₃ (yttria) which forms a solid solution in the ZrO₂ lattice. Materials, in which the stabilization of the high-temperature phase is attained by means of an yttria addition, are conventionally called yttria-stabilized zirconia (YSZ) [4]. An amount of ≈ 3 mol. % of the Y₂O₃ is sufficient to stabilize the tetragonal ZrO₂ phase down to ambient temperature. The high temperature cubic phase of YSZ is stabilized at room temperature by adding more than ≈ 8 mol. % of the Y₂O₃ stabilizer to zirconia.
The present work presents characterization of radiation-induced defects in YSZ implanted by heavy Xe ions with energy of 167 MeV. To examine the effect of microstructure on the radiation hardness two YSZ samples with different microstructure were compared: (i) single crystal and (ii) sintered ceramic. Positron annihilation spectroscopy (PAS) was employed for characterization of defects created by Xe implantation. PAS investigations were combined with optical measurements.

2. Experimental
A ZrO$_2$ + 10 mol.% Y$_2$O$_3$ (110) single crystal with cubic structure and tetragonal ZrO$_2$ + 3 mol.% Y$_2$O$_3$ ceramic sintered at 1350°C were studied. The ceramics exhibits the mean grain size of ~ 250 nm. In the following text these samples are denoted YSZ10 and YSZ3, respectively. Both samples were implanted by Xe$^{26+}$ ions with energy of 167 MeV up to a fluence of $3 \times 10^{12}$ cm$^{-2}$. The Xe irradiations were made at IC-100 FLNR cyclotron in JINR, Dubna. The temperature of the samples during Xe irradiation did not exceed 50 °C.

PAS investigations were performed using a $^{22}$NaCO$_3$ positron source with activity of 1 MBq deposited on 2 μm thick mylar foil. A digital spectrometer [5] with time resolution of 145 ps (FWHM of resolution function) was employed for positron lifetime (LT) spectroscopy. At least $10^7$ positron annihilation events were collected in each LT spectrum which was decomposed into exponential components by a maximum likelihood code [6]. Contribution of annihilations from positron source was derived on the basis of reference LT measurements with a well-annealed α-Fe sample with intensity adjusted for YSZ according to the procedure suggested in Ref. [7]. The source contribution consisted of two components with lifetimes 368 ps and 1.5 ns and corresponding relative intensities 7 and 1%. Coincidence Doppler broadening (CDB) investigations were carried out using a digital spectrometer [8] equipped with two HPGe detectors. At least $10^8$ positron annihilation events were accumulated in each CDB spectra.

3. Theoretical calculations
Ab-initio calculations of positron lifetimes were performed within the so-called standard scheme [9] employing the atomic superposition (ATSUP) method [10]. The electron–positron correlation was treated using the local density approximation (LDA) according to the parametrization by Boroński and Nieminen [11] taking into account incomplete positron screening [12] considering the high-frequency dielectric constant as $\varepsilon_{\infty} = 4.62$. The calculations were performed for 768 atom based supercells. Point defects (vacancies and vacancy clusters) were modeled by removing the corresponding number of Zr or O atoms from the supercell.

4. Results and discussion
4.1. Virgin samples
Results of LT investigations for the virgin samples are collected in Table 1. The YSZ10 sample exhibits a single component LT spectrum with lifetime of $\approx 179$ ps which is significantly higher than the zirconia bulk lifetime [13]. Hence, the YSZ10 exhibits high concentration of defects already in the virgin state and virtually all positrons are annihilated in the trapped state. The lifetime of 179 ps can be attributed to positrons trapped at defects with open volume comparable to zirconium vacancy (V$_{Zr}$) [13]. High density of defects in the as-grown YSZ single crystal was confirmed also by positron back-diffusion measurement performed using a variable energy slow positron beam which yielded very short positron diffusion length of $\approx 9$ nm only [13]. Note that theoretical ab-initio calculations performed in Ref. [13] revealed that V$_{Zr}$ are deep positron traps but oxygen vacancies (V$_O$) are incapable of positron trapping at room temperature.

The virgin YSZ3 sample exhibits more complicated LT spectrum consisting of three components listed in Table 1. The short-lived component with lifetime $\tau_1 \approx 40$ ps comes from free positrons not trapped at defects. The dominating component with lifetime $\tau_2 \approx 176$ ps (relative intensity $I_2 \approx 88\%$)
can be attributed to vacancy like defects similar to those in the virgin YSZ single crystal. The long-lived component with lifetime $\tau_3 \approx 320$ ps represents a contribution of positrons trapped at larger point defects with open volume corresponding to several vacancies. As shown in Ref. [13] these larger point defects are located at triple points, i.e. intersections of three of more grain boundaries. Considerable intensity ($I_3 \approx 7\%$) of positrons trapped at triple points is due very small grain size ($\approx 250$ nm) of the sintered ceramic. The effect of sintering on microstructure of YSZ ceramic was studied in Ref. [14] using variable energy slow positron beam. The density of defects strongly decreases during sintering which was revealed by lowered $S$ parameter and also by more gradual decrease of $S$ from the surface to bulk. However, determination of the mean positron diffusion length was found to be difficult since the microstructure of sintered ceramic became non-homogeneous and defect density decreased from the surface towards bulk [14]. The positron diffusion length of $\approx 15$ nm estimated in the sub-surface region of the ceramic sintered at $1350^\circ C$ can be considered as a lower bound. The mean positron diffusion length in bulk is definitely higher. Hence assuming $L_+ \approx 15$ nm as a lower bound of the positron diffusion length and the mean grain size of $d \approx 250$ nm the fraction of positrons which can reach grain boundaries containing triple points by diffusion can be roughly estimated as $1 - (d - L_+)^2/d^2 \approx 12\%$. Taking into account that grain boundaries are defects with large cross-section for positron trapping one can expect that larger portion of these positrons will be trapped at triple points. This is in accordance with considerable intensity $I_3 \approx 7\%$ of positrons trapped at triple points resolved here in the LT spectrum of the virgin YSZ3 sintered ceramic. Note that for nanocrystalline YSZ samples which exhibit even smaller grain sizes the intensity of positrons trapped at triple points was correspondingly higher [13].

Table 1. Results of LT investigations: lifetimes $\tau_i$ and relative intensities $I_i$ of the components resolved in LT spectra. The standard deviations are given in parentheses in the units of the last significant digit.

| sample                      | $\tau_1$ (ps) | $I_1$ (%) | $\tau_2$ (ps) | $I_2$ (%) | $\tau_3$ (ps) | $I_3$ (%) |
|-----------------------------|---------------|-----------|---------------|-----------|---------------|-----------|
| YSZ10: ZrO$_2$ + 10 mol.% Y$_2$O$_3$ (110) single crystal |               |           |               |           |               |           |
| virgin                      | -             | -         | 178.5(1)      | 100       | -             | -         |
| Xe-implanted                | -             | -         | 178.1(7)      | 95.1(6)   | 370(10)       | 4.9(5)    |
| YSZ3: ZrO$_2$ + 3 mol.% Y$_2$O$_3$ sintered ceramic |               |           |               |           |               |           |
| virgin                      | 40(10)        | 5(2)      | 176(2)        | 88(1)     | 322(9)        | 7.0(6)    |
| Xe-implanted                | -             | -         | 177.6(8)      | 90.5(7)   | 355(8)        | 9.5(6)    |

4.2. Xe-implanted samples

Implantation of 167 MeV Xe ions into zirconia target was simulated by the SRIM code [15] and results are plotted in Fig. 1. The depth profile of Xe ions is plotted by solid line in the figure while shaded area shows the depth profile of vacancies created by implantation. The stopping depth of Xe ions into zirconia is $z_{Xe} \approx 10.8$ nm. For the ion fluence of $3 \times 10^{12}$ cm$^{-2}$ used here the damage dose at the peak of the damage distribution is $\approx 0.019$ dpa. In Fig. 1 the depth profile of Xe ions is compared with the implantation profile of positrons emitted by $^{22}$Na radioisotope (dashed line). The positron implantation profile can be described by exponential function [16]

$$p(z) = \frac{1}{z_0} \exp \left( -\frac{z}{z_0} \right),$$

where $z$ is the depth from the surface. The mean positron penetration depth $z_0$ can be expressed as
\[ z_0 = \frac{E_{\text{max}}^{1.4}}{16 \rho}. \]  

(2)

The symbol \( \rho \) in the above equation stands for the density of the sample (expressed in g cm\(^{-3} \)) and \( E_{\text{max}} \) is the end-point energy of the emitted positrons (expressed in MeV). The mean penetration depth of the positrons emitted by the \( ^{22}\text{Na} \) radioisotope (\( E_{\text{max}} = 0.545 \) MeV) into zirconia is 48 \( \mu \text{m} \). The probability \( P \) that a positron emitted by \( ^{22}\text{Na} \) source is stopped in the layer modified by Xe implantation is obtained by integrating the positron implantation profile

\[
P = \int \frac{1}{z_0} \exp \left( -\frac{z}{z_0} \right) dz.
\]

(3)

For Xe-implanted YSZ specimens Eq. (3) yielded \( P = 20\% \). Hence, considerable fraction of positrons is annihilated in the layer affected by Xe implantation.

The YSZ10 single crystal implanted by Xe ions exhibit two-component LT spectrum, see Table 1. The dominating contribution comes again from V\(_Zr\) which represented the dominating kind of positron traps also in the virgin crystal. A new component with lifetime \( \tau_3 \approx 370 \) ps which appeared in LT spectrum of the implanted crystal can be attributed to positrons trapped at larger point defects with open volume corresponding to several vacancies. Bombarding high energy Xe ions create high number of vacancies in zirconia, see Fig. 1. SRIM simulations revealed that on average \( \sim 19000 \) vacancies (both V\(_Zr\) and V\(_O\)) are created by each Xe ion. Since implantation is performed at room temperature most of these vacancies are annealed, i.e. they either recombine with interstitials or disappear by diffusion to sinks at grain boundaries. However, some irradiation-induced vacancies agglomerate into vacancy clusters. Because of saturated trapping monovacancies created by implantation cannot be distinguished from those present already in the virgin crystal. But irradiation-induced vacancy clusters can be distinguished and led to rise of the long-lived component with the lifetime \( \tau_3 \) in the implanted crystal. It has to be noted that annealing of vacancies is not considered in SRIM simulations, i.e. Fig. 1 shows the concentration of vacancies created during implantation but not the concentration of vacancies survived in the irradiated sample at room temperature.

**Figure 1.** Results of SRIM simulations for 167 MeV Xe ions implantation into zirconia: the depth profiles of implanted Xe ions (\( c_{\text{Xe}} \), blue solid line) and vacancies created by implantation (\( c_v \), filed grey area). Dashed line shows the implantation profile of positrons emitted by \( ^{22}\text{Na} \) radioisotope.
Ab-initio theoretical calculations were employed for determination of the average size of vacancy clusters created by Xe irradiation. Calculated positron lifetimes for vacancy clusters of various sizes are plotted Fig. 2 as a function of the effective cluster ‘size’ calculated as \( n_{VZr} d_{Zr} + n_{VO} d_{O} \), where \( n_{VZr} \) and \( n_{VO} \) is the number of V\(_{Zr}\) and V\(_{O}\) in the cluster and \( d_{Zr} \) and \( d_{O} \) is the diameter of Zr and O atom, respectively. From inspection of Fig. 2 it becomes clear that the lifetime \( \tau_3 \approx 370 \) ps observed in the Xe-implanted crystal corresponds to vacancy clusters consisting of 6 V\(_{Zr}\) and 6 V\(_{O}\) (6V\(_{Zr}\)+6V\(_{O}\)). Note that the lifetime for vacancy clusters in Xe-implanted crystal is remarkable higher than the lifetime of 312 ps reported for YSZ implanted by 2 MeV He ions [17]. The lifetime of 312 ps measured in the He implanted YSZ corresponds to vacancy clusters consisting of 4 V\(_{Zr}\) and 4 V\(_{O}\) (4V\(_{Zr}\)+4V\(_{O}\)), see Fig. 2. Hence, irradiation by heavy Xe ions with high energy created larger vacancy clusters than irradiation by lighter and lower energy He ions.

The YSZ3 ceramic implanted by Xe ions exhibits saturated positron trapping at V\(_{Zr}\) (lifetime \( \tau_2 \approx 178 \) ps) and larger point defects characterized by the lifetime \( \tau_3 \approx 355 \) ps, see Table 1. Disappearance of the free positron component testifies that the concentration of defects in the Xe-implanted ceramic increased. Moreover, the lifetime \( \tau_3 \) is enhanced and the intensity \( I_3 \) is increased with respect to the virgin ceramic. This testifies that in the Xe-implanted ceramic the long-lived component with lifetime \( \tau_3 \) represents a contribution of positrons trapped at triple points (lifetime \( \approx 320 \) ps) which are present already in the virgin sample and also vacancy clusters (lifetime \( \approx 370 \) ps) created by Xe irradiation.

![Figure 2](image-url)

**Figure 2.** Results of *ab-initio* theoretical calculations of positron lifetimes for various defects in zirconia. Labels show the number of Zr-vacancies (V\(_{Zr}\)) and O-vacancies (V\(_{O}\)) forming the cluster. Positron lifetimes are plotted versus the effective ‘size’ of defects, see text.

Results of CDB investigations are presented in Fig. 3 as ratio curves with respect to well annealed pure Zr. The ratio curves for the virgin and Xe-implanted YSZ10 crystal and YSZ3 ceramic are
compared in Fig. 3a and 3b, respectively. The prominent feature of all ratio curves measured is a pronounced peak at $p \approx 15 \times 10^{-3} \text{m}_0c$ which represents a contribution of positrons annihilated by $2p$ oxygen electrons [13]. The ratio curves for YSZ10 and YSZ3 samples are very similar and the contribution of positrons annihilated by oxygen electrons is significantly higher than in YSZ nanopowders measured in Ref. [13]. This is in agreement with LT investigations which identified $V_{Zr}$ as dominant positron traps. Since oxygen anions are the nearest neighbours of $V_{Zr}$, the high momentum part of the momentum distribution of positrons trapped at $V_{Zr}$ contains prominent contribution from positrons annihilated by oxygen electrons. One can see in Fig. 3 that the ratio curves for YSZ10 and YSZ3 samples implanted by Xe ions are almost the same as those for the corresponding virgin materials. This indicates in accordance with LT studies that $V_{Zr}$ remain the dominating positron traps also in the Xe-implanted samples.

Fig. 4a shows optical transmittance of the virgin and Xe-implanted YSZ10 crystal. The virgin crystal is colourless and transparent in the whole spectrum of the visible light. Implantation by Xe ions turned the crystal grey and a broad minimum appeared in the optical transmittance curve. This gives clear evidence that defects providing electron states in the band gap and allowing for absorption of visible light were created by Xe-implantation. The difference between optical transmittance of the Xe-implanted and the virgin YSZ10 crystal is plotted in Fig. 4b. Obviously the Xe-implanted crystal absorbs light in a broad range of wavelengths 350-650 nm. Similar broad absorption band has been reported in a cubic $\text{ZrO}_2 + 9.5$ mol.% $\text{Y}_2\text{O}_3$ single crystal implanted by 200 keV $\text{Xe}^+$ ions [18]. However, the absorption band was observed only after irradiation up to the Xe ion fluence of $10^{16} \text{cm}^{-2}$ or higher [18]. Here the absorption band was observed already at significantly lower fluence of $3 \times 10^{12} \text{cm}^{-2}$ due to much higher energy of implanted Xe ions. The broad absorption band was previously observed in X-ray irradiated YSZ sample and has been attributed to two types of defects: (i) $V_{O}$ with trapped electron (F-type centre) and (ii) hole-trapped oxygen ion (V-type centre) adjacent to yttrium cation [19]. Since Xe implantation produces large number of $V_{O}$, explanation of the broad absorption band by irradiation-induced F-type centres is very plausible. Note that the absorption band in Fig. 4 exhibits maximum absorption at 518 nm. This is very similar to the peak of the absorption band of 522 nm observed in Xe-implanted YSZ in Ref. [18] but it is shifted to longer wavelength compared the peak of absorption band in X-ray irradiated YSZ (465 nm) [19] and neutron irradiated YSZ (470 nm) [20]. It has been suggested that this red shift could be due to aggregation of vacancies to vacancy clusters [18,21]. Our positron lifetime investigations support this hypothesis. Since irradiation by Xe ions leads higher density of $V_{O}$ per track length compared to X-rays or neutrons used in Refs. [19,20] the agglomeration of $V_{O}$ into clusters becomes easier.

**Figure 3.** CDB ratio curves (with respect to well annealed pure Zr) for (a) virgin and Xe-implanted YSZ10 crystal and (b) virgin and Xe-implanted YSZ3 ceramic.
Figure 4. Results of optical measurements of YSZ10 crystal: (a) transmittance of the virgin and Xe-implanted crystal; (b) difference between the optical transmittance curves.

Change of coloration caused by Xe implantation was observed also in YSZ3 ceramic. The virgin ceramic was white as shown Fig. 5a but after implantation by Xe ions it turned pink, see Fig. 5b. Similarly to YSZ10 crystal the change of colour of Xe-implanted YSZ3 ceramic is caused by irradiation-induced colour centres.

5. Conclusions
A cubic ZrO$_2$ + 10 mol.% Y$_2$O$_3$ single crystal and tetragonal ZrO$_2$ + 3 mol.% Y$_2$O$_3$ ceramic were implanted by 167 MeV Xe ions. Defects in the virgin and Xe-implanted samples were characterized by positron annihilation spectroscopy. Both the single crystal and the ceramic sample exhibit V$_{Zr}$ as dominating positron traps in the virgin state. The virgin samples contain most probably also V$_O$ but they are not able to confine positrons. Irradiation by Xe ions introduced larger point defects characterized by positron lifetime of $\approx$ 370 ps and identified as clusters consisting of 6 V$_{Zr}$ and 6 V$_O$. Xe-implantation introduced colour centres and changed colour of both the single crystal (colourless to grey) and the ceramic (white to pink). Measurement of optical transmittance of Xe-implanted single crystal revealed a wide absorption band (350-650 nm) which is likely caused by irradiation-induced F-type centres.

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References
[1] Li P, Chen I W, James E and Hahn J E P 1993 Phys. Rev. B 48 10063
[2] van Duppen P, Decrock P, Huyse M, Delbar Th, Galster W, Leleux P, Lienard I, Lipnik P, Loiselet M, Michotte C, Ryckewaert G, Vervier J, Duhamel P and Vanhorenbeeck J 1992 Nucl. Instr. Meth. B 70 393
[3] Evans A G and Cannon R M 1986 Acta Metall. 34 761
[4] Yanagida H, Kounoto K, and Miyayama M 1996 The Chemistry of Ceramics (Chichester, John Wiley & Sons)
[5] Bečvář F, Čížek J, Prochážka I and Janotová J 2005 Nucl. Instrum. Methods A 539 372
[6] Prochážka I, Novotný I, Bečvář F 1997 Mater. Sci. Forum 255-257 772
[7] Surbeck H 1977 Helv. Phys. Acta 50 705
[8] Čížek J, Vlček M and Prochážka I 2010 Nucl. Instr. Meth. in Phys. Research A 623 982
[9] Puska M J and Nieminen R M 1994 Rev. Mod. Phys. 66 841
[10] Puska M J and Nieminen R M 1983 J. Phys. F 13 333
[11] Borofski E and Nieminen R M 1986 Phys. Rev. B 34 3820
[12] Puska M J, Mäkinen S, Manninen M and Nieminen R M 1989 Phys. Rev. B 39 7666
[13] Čížek J, Melikhova O, Prochážka I, Kuriplach J, Kužel R, Brauer G, Anwand W, Konstantinova T E and Danilenko I A 2010 Phys. Rev. B 81 024116
[14] Prochážka I, Čížek J, Melikhova O, Anwand W, Brauer G, Konstantinova T E and Danilenko I A 2013 Mater. Sci. Forum 733 236
[15] Ziegler J F, Ziegler M D and Biersack J P 2010 Nucl. Instr. Meth. in Phys. Research B 268 1818
[16] Hautojärvi P and Corbel C 1995 Positron Spectroscopy of Solids Proc. Int. School of Physics ‘Enrico Fermi’ ed A Dupasquier and A P Mills (Amsterdam: IOS Press) p 491
[17] Grynszpan R I, Brauer G, Anwand W, Malaquin L, Saudé S, Vickridge I and Briand E 2007 Nucl. Instr. Meth. in Physics Research B 261 888
[18] Zhu S, Zu X T, Xiang X, Wang Z G, Wang L M and Ewing R C 2003 Nucl. Instr. Meth. in Physics Research B 206 1092
[19] Orera V M, Merino R I, Chen Y, Cases R and Alonso P J 1990 Phys. Rev. B 42 9782
[20] Savoini B, Cáceres D C, Vergara I, González R and Muñoz Santiuste J E 2000 J. Nucl. Mater. 277 199
[21] Grinyaev S N, Konusov F V and Lopatin V V 2002 Phys. Solid State 44 275