Defect Studies of Zirconia Implanted by High Energy Xe Ions

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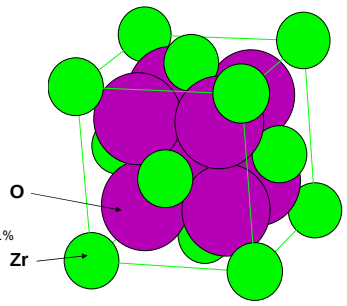
Introduction

Zirconia (ZrO_2)
- wide band gap insulator (5-7 eV)
- high melting point 2700ºC
- radiation hard material
- high temperature applications
- three ZrO_2 polymorphs
  - monoclinic < 1200ºC
  - tetragonal 1200ºC – 1380ºC
  - cubic > 1380ºC

yttria stabilized zirconia ($ZrO_2 + xY_2O_3$)
- tetragonal phase is stabilized down to RT for $x \approx 3$ mol.%
- cubic phase is stable at RT for $x > 8$ mol.%

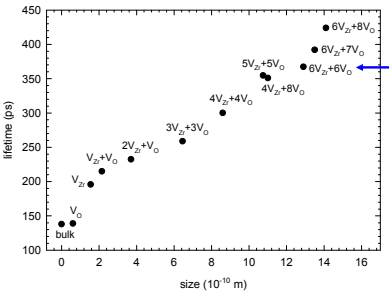


Structure of cubic ZrO_2

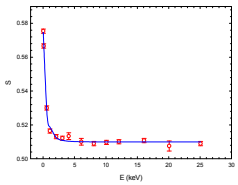
Theoretical calculations

- Positron lifetimes were calculated by density functional theory (DFT)
- Standard scheme: the limit of vanishing positron density [Puska94].
- Electron-positron correlations treated within local density approximation (LDA) using a parametrization by Boronsky and Nieminen [Boronski86] with correction for incomplete screening [Puska89] using the dielectric constant $\varepsilon = 4.62$
- The effective potential for positrons constructed by atomic superposition (ATSUP) [Puska83]
- cubic ZrO_2 phase $a = 5.08$ Å
- 768 atom base supercells (256 Zr + 512 O)
- atomic relaxation around defects not considered

Results
- bulk lifetime: 138 ps (within GGA scheme 151 ps)
- Oxygen vacancy (V_O): 139 ps, do not trap positrons ($E_b = 0.05$ eV)
- Zirconium vacancy (V_{Zr}): 196 ps, deep positron trap ($E_b = 2.33$ eV)
- experimental lifetime of 370 ps measured in Xe implanted crystal corresponds to a cluster consisting of $6V_{Zr}$ and $6V_O$ ($6V_{Zr}+6V_O$)

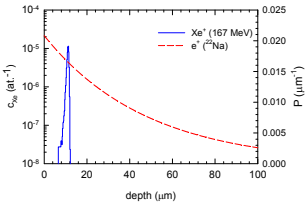


Calculated positron lifetimes for vacancy clusters of various sizes in ZrO_2



Dependence of S parameter on energy of incident positrons for virgin $ZrO_2 + 10\%Y_2O_3$ single crystal

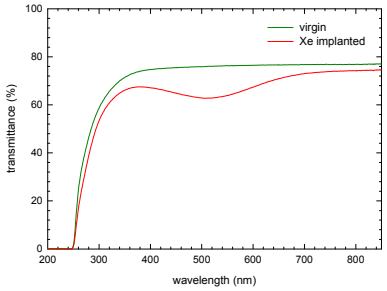
experiment (Xe implanted ZrO_2+10%Y_2O_3 single crystal)



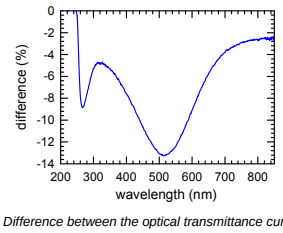
Comparison of implantation profile of 167 MeV Xe ions (blue) calculated by SRIM and positron implantation profile (red)

Optical measurements

- virgin $ZrO_2 + 10\%Y_2O_3$ single crystal is transparent with high transmittance in the whole spectrum of visible light
- after Xe implantation the crystal becomes pinkish
- Xe implantation induced color centers with maximum absorption at wavelength of 520 nm
- $ZrO_2 + 3\%Y_2O_3$ ceramic changed its color from white to pink after Xe implantation as well

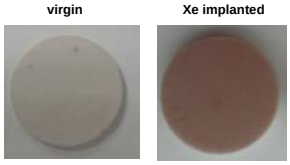


Optical transmittance for virgin and Xe implanted $ZrO_2 + 10\%Y_2O_3$ single crystal.



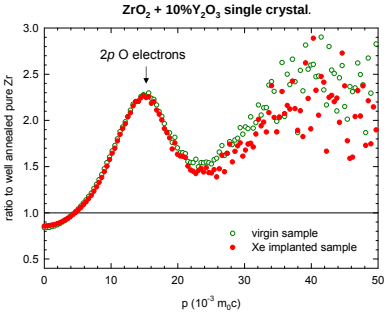
Difference between the optical transmittance curves.

$ZrO_2 + 3\%Y_2O_3$ ceramic



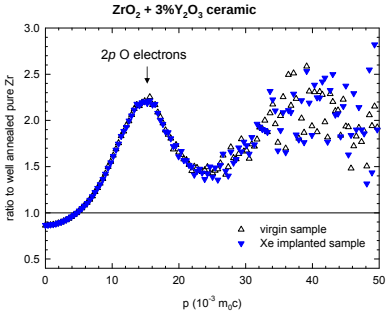
Change of coloration of $ZrO_2 + 3\%Y_2O_3$ ceramic after Xe implantation .

$ZrO_2 + 10\%Y_2O_3$ single crystal.

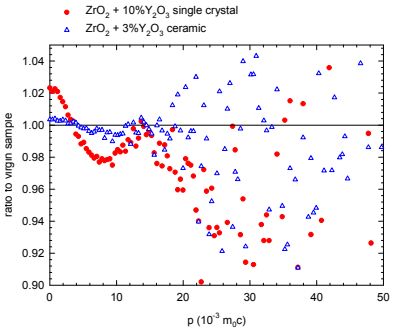


CDB ratio curves (with respect to well annealed Zr) for virgin and Xe implanted $ZrO_2 + 10\%Y_2O_3$ single crystal.

$ZrO_2 + 3\%Y_2O_3$ ceramic



CDB ratio curves (with respect to well annealed Zr) for virgin and Xe implanted $ZrO_2 + 3\%Y_2O_3$ ceramic.



CDB ratio curves showing ratio of Xe implanted versus virgin sample

Experimental

Samples
- $ZrO_2 + 10\%Y_2O_3$ single (110) crystal, cubic structure
- $ZrO_2 + 3\%Y_2O_3$ sintered ceramic, $T_s = 1350$ºC, tetragonal structure

Ion implantation
- Xe^{26+} ions, E = 167 MeV, fluence: 3×10^{13} cm^{-2}, temperature T < 50ºC, JINR Dubna
- stopping range in ZrO_2: 10.8 μm

Positron annihilation spectroscopy
- positron source: ^{22}Na with activity 1 MBq deposited on 2 μm thick mylar foil
- digital positron lifetime spectrometer [Becvar05], time resolution 145 ps (FWHM ^{22}Na), 10^7 annihilation events in spectra
- digital coincidence Doppler broadening spectrometer [Cizek10a], resolution 0.9 keV at 511 keV, 10^8 annihilation events in spectra

Optical measurements
- measurememnt of optical transmittance in the wavelength range 200 – 900 nm at room temperature

Positron Lifetime (LT) Spectroscopy

Virgin samples
- **$ZrO_2 + 10\%Y_2O_3$ single crystal**
- virgin $ZrO_2 + 10\%Y_2O_3$ single (110) crystal exhibits single component spectrum with lifetime 178.5 ps, which is considerably higher than the bulk lifetime
- saturated trapping at Zr-vacancies (V_{Zr})
- experimental lifetime is shorter than lifetime calculated for V_{Zr} (196 ps) most probably due to inward relaxation of neighbouring ions
- high density of defects in the virgin crystal was confirmed also by measurement on the slow positron beam [Cizek10b] → very short positron difusion length $L_+ = (8.6 \pm 0.4)$ nm
- **$ZrO_2 + 3\%Y_2O_3$ ceramic**
- virgin $ZrO_2 + 3\%Y_2O_3$ ceramic exhibits 3-component spectrum containing (i) free positron component $\tau_1 \approx 40$ ps, (ii) positrons trapped at V_{Zr}, $\tau_2 \approx 176$ ps, (iii) positrons trapped at triple points (intersection of three or more grain boundaries), $\tau_3 \approx 320$ ps

	free positrons		Zr-vacancies		vacancy clusters	
sample	**τ_1 (ps)**	**I_1(%)**	**τ_2 (ps)**	**I_2(%)**	**τ_3 (ps)**	**I_3(%)**
ZrO_2 +10% Y_2O_3 (110) single crystal						
virgin	-	-	178.5(1)	100	-	-
Xe implanted	-	-	178.1(7)	95.1(6)	370(10)	4.9(5)
ZrO_2 +3% Y_2O_3 sintered ceramic						
virgin	40(10)	5(2)	176(2)	88(1)	322(9)	7.0(6)
Xe implanted	-	-	177.6(8)	93.5(7)	355(8)	9.5(5)

Xe implanted samples
- stopping depth of 167 MeV Xe ions in ZrO_2 is $z_{Xe} = 10.8$ mm (SRIM simulation)
- positron implantation profile: $p(z) = \frac{1}{z_0}\exp\left(-\frac{z}{z_0}\right)$ the mean positron penetration depth for ZrO_2: $z_0 = \frac{E_{max}^{1.6}}{16\rho} = 48\ \mu m$ $E_{max} = 0.545$ MeV, ρ - density
- probability that positron is stopped in the layer affected by Xe implantation: $P = \int_0^{z_{Xe}} p(z)dz = 1 - \exp\left(-\frac{z_{Xe}}{z_0}\right) = 20\%$

- **$ZrO_2 + 10\%Y_2O_3$ single crystal**
- long lived component with lifetime $\tau_3 \approx 370$ ps appeared in LT spectrum
- contribution of positrons trapped at vacancy clusters created by bombarding Xe ions
- experimental lifetime of irradiation-induced vacancy clusters correspond to clusters consisting of $6V_{Zr}$ and $6V_O$ ($6V_{Zr}+6V_O$)
- **$ZrO_2 + 3\%Y_2O_3$ ceramic**
- lifetime τ_3 of the long lived component was prolonged and its intensity increased
- this is due to irradiation-induced $6V_{Zr}+6V_O$ clusters which contribute to the component τ_3
- hence in Xe implanted ceramic the component with lifetime τ_3 contains a contribution from positrons trapped at triple points existing already in the virgin sample and a contribution of positrons trapped at irradiation-induced $6V_{Zr}+6V_O$ clusters

Coincidence Doppler broadening (CDB)

- CDB ratio curves (with respect to pure annealed Zr): peak at $p \approx 15 \times 10^{-3}$ m_0c comes from 2*p* O electrons
- $ZrO_2 + 10\%Y_2O_3$ single crystal: Xe implantation leads to only a slight decrease of the fraction of positrons annihilated by oxygen electrons
- $ZrO_2 + 3\%Y_2O_3$ ceramic: practically no change of CDB ratio curve after Xe implantation
- Hence chemical environment of clusters created by Xe-implantation is similar to defects present in the virgin samples
- Xe bubbles were not detected due to low concentration of implanted Xe

Conclusions

- Cubic $ZrO_2 + 10\%Y_2O_3$ single crystal and tetragonal $ZrO_2 + 3\%Y_2O_3$ ceramic were implanted by 167 Xe ions.
- Virgin $ZrO_2 + 10\%Y_2O_3$ single crystal exhibits saturated trapping in V_{Zr}
- In virgin $ZrO_2 + 3\%Y_2O_3$ ceramic positrons are trapped at V_{Zr} and at larger point defects at triple points
- Both in the single crystal and the ceramic Xe implantation created clusters consisting of $6V_{Zr}$ and $6V_O$.
- Chemical environment of irradiation-induced clusters is similar to defects in virgin samples.
- Optical measurements revealed that Xe implantation created colour centres with maximum absorption at the wavelength of 520 nm.

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