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Characterization of point defects in yttria stabilized zirconia single crystals

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Abstract. Characterization of point defects in a fully stabilized ZrO_2 + 9 mol.% Y_2O_3 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 (ZrO_2) 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 (Y_2O_3) [2]. Such a system is then called yttria stabilized zirconia (YSZ). An embedment of Y_2O_3 into the ZrO_2 host lattice leads to a deviation from stoichiometry resulting in the creation of a high amount of native oxygen vacancies (V_O). 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

ZrO_2 + 9 mol.% Y_2O_3 single crystal with (100) orientation and dimensions $10 \times 10 \times 0.5$ mm^3 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 ^{22}Na) 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 $^{15}N + {}^{1}H \rightarrow {}^{12}C + {}^{4}He + \gamma$ rays. The hydrogen concentration was determined at a sample depth of ~ 100 nm using ^{15}N ions accelerated to 6.64 MeV.

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

Table 1. Results of *ab-initio* theoretical calculations of positron parameters: bulk positron lifetime for ZrO_2 crystal, positron lifetimes τ 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}+ *n*H).

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 2×2×2 *k*-mesh sampling centered at the Γ 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.

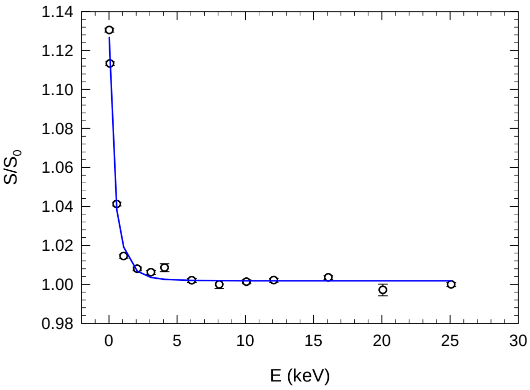

Figure 1. Dependence of the *S* parameter (open circles) on the positron energy the *E* for the ZrO_2 + 9 mol.%Y_2O_3 single crystal. The *S* parameter was normalized to the bulk value S_0 measured at *E* = 25 keV. The solid line shows a model curve fitted by the VEPFIT [10].

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 ± 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

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

where τ_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 τ_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.%).

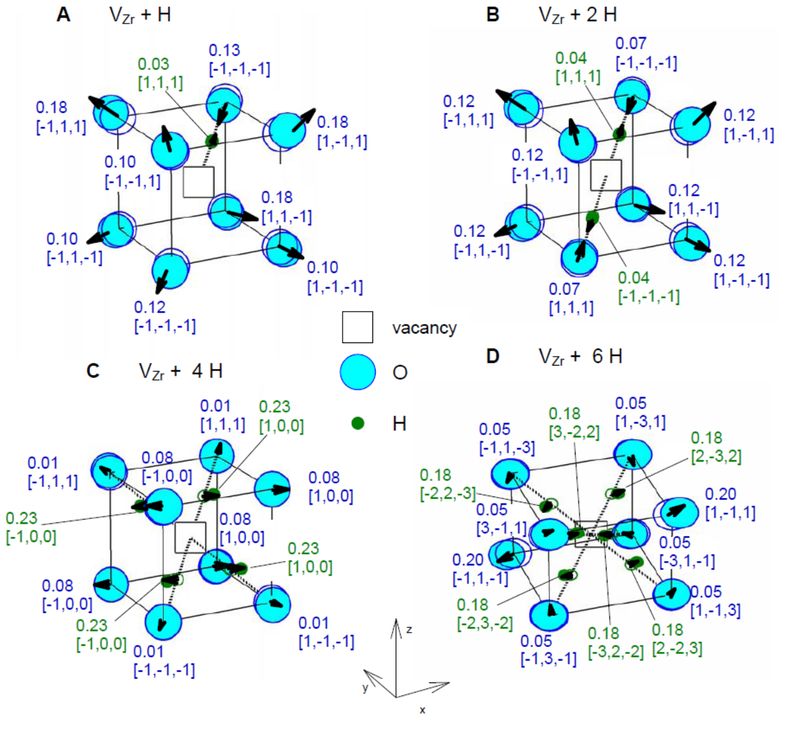

Figure 2. Relaxed geometries for V_{Zr} associated with various number of hydrogen atoms (V_{Zr} + *n*H). Relaxed positions of the nearest neighbour O atoms and trapped H atoms are shown by filled symbols, while open symbols show positions in the rigid lattice. The values in the figure are displacement 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 V_O 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 (V_{Zr}), which is a deep positron trap [8,11].

However, one can see in the table 1 that calculated lifetime of positrons trapped in V_{Zr} is longer than 175 ps determined in experiment. Note that Damonte et al. [12] found in ZrO_2 + 8 mol.% Y_2O_3 crystal a component with lifetime of 196 ps, i.e. again shorter lifetime than that calculated for V_{Zr}. A shortening of the positron lifetime may be caused by some impurity associated with V_{Zr} 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 ± 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

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