Evidence of excess oxygen accommodation in yttria partially-stabilized zirconia
Middleburgh, Simon C.; Ipatova, Iuliia; Evitts, Lee J.; Rushton, Michael J.D.; Assinder, Ben; Grimes, Robin W.; Lee, William E.
SCRIPTA MATERIALIA

DOI: 10.1016/j.scriptamat.2019.08.040

Published: 15/01/2020

Publisher's PDF, also known as Version of record

Cyswllt i'r cyhoeddiad / Link to publication

Dyfniad o’r fersiwn a gyhoeddwyd / Citation for published version (APA):

Hawliau Cyffredinol / General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

14. Feb. 2020
Evidence of excess oxygen accommodation in yttria partially-stabilized zirconia

Simon C. Middleburgh a,⁎, Iuliia Ipatova a, Lee J. Evitts a, Michael J.D. Rushton a, Ben Assinder b, Robin W. Grimes c, William E. Lee a,c

a Nuclear Futures Institute, Bangor University, Bangor LL57 1UT, United Kingdom
b School of Electronic Engineering, Bangor University, LL57 1UT, United Kingdom
c Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom

A R T I C L E   I N F O

Article history:
Received 24 July 2019
Received in revised form 19 August 2019
Accepted 30 August 2019
Available online xxxx

Keywords:
Non-stoichiometry
Yttria partially stabilized zirconia
Raman spectroscopy
Density functional theory
Peroxide ion defect

A B S T R A C T

Yttria partially stabilized zirconia (ZrO2)(Y2O3)½−x has been investigated to understand accommodation of excess oxygen into its structure. ZrO2 powder with 8 wt% Y2O3 additions was treated in 30 vol% H2O2 solution to promote oxidation of the material. A new Raman peak was observed after treatment at 840 cm−1, consistent with previous reports of solid state peroxide ions (O22−). This was corroborated using atomic scale simulation based on density functional theory; these also highlighted the near-zero solution enthalpy for excess oxygen in the monoclinic structure via the formation of a peroxide ion defect.

© 2019 Published by Elsevier Ltd on behalf of Acta Materialia Inc.
patterns of the as-received material were obtained using a PANalytical Aeris X-ray diffractometer with Cu-Kα radiation (λ = 1.5406 Å, voltage = 40 kV and current = 7.5 mA) and are reported in Fig. 1. Scans were taken in the 2θ range 10° to 80° at increments of 0.01° with a time-step of 60 s. The X-ray diffraction (XRD) analysis of the as-received YSZ-8 sample demonstrates the existence of two crystalline phases: primarily a tetragonal phase (60%) with the remainder made up of the monoclinic phase (using the same methodology for crystal phase identification first used by Toraya et al. [14]), consistent with previous examinations of this compound [15,16,17]. A finer X-ray diffraction pattern was obtained on the same material between 72 and 76° to verify the c/a ratio of the tetragonal phase in order to identify its nature (either the equilibrium phase or the metastable form). Two peaks were observed in this range at 73.13° and 74.35°, identified as the (004) and (220) peaks of the tetragonal phase [18] giving lattice parameters of a = b = 5.607 Å and c = 5.173 Å. This gives a /a \sqrt{2} of 1.014, indicating that the tetragonal phase resides within the transformable tetragonal phase as described by Viazzi et al. [18] which also corresponds to a Yo1.5 content of 6.4 mol%.

The as-received material was heated to 1200 °C for 2 h and then rapidly cooled in air back to room temperature. The resulting X-ray diffraction pattern showed a marked increase of the tetragonal phase to 95% (the remainder being monoclinic). The peak positions between 72 and 76° did not shift, as is expected in the non-equilibrium phase diagram according to Chevalier and Gremillard [19] and Fabrichnaya and Aldinger [20].

To understand the potential for excess oxygen accommodation, the powder was treated in 30 vol% H2O2 solution for 1 day and 1 week at 5 °C before rinsing in deionized water and drying on filter paper for 24 h at room temperature (similar to [9]).

Raman spectra were obtained using a Bruker Senterra 2 instrument equipped with a 532 nm laser. The laser power was 25 mW and a 50 μm aperture was used. An integration time of 5 s was applied with 5 co-additions. The stated spectral resolution was 4 cm⁻¹ to verify the c/a ratio of the tetragonal phase in order to identify its nature (either the equilibrium phase or the metastable form). Two peaks were observed in this range at 73.13° and 74.35°, identified as the (004) and (220) peaks of the tetragonal phase [18] giving lattice parameters of a = b = 5.607 Å and c = 5.173 Å. This gives a /a \sqrt{2} of 1.014, indicating that the tetragonal phase resides within the transformable tetragonal phase as described by Viazzi et al. [18] which also corresponds to a Yo1.5 content of 6.4 mol%.

The as-received material was heated to 1200 °C for 2 h and then rapidly cooled in air back to room temperature. The resulting X-ray diffraction pattern showed a marked increase of the tetragonal phase to 95% (the remainder being monoclinic). The peak positions between 72 and 76° did not shift, as is expected in the non-equilibrium phase diagram according to Chevalier and Gremillard [19] and Fabrichnaya and Aldinger [20].

To understand the potential for excess oxygen accommodation, the powder was treated in 30 vol% H2O2 solution for 1 day and 1 week at 5 °C before rinsing in deionized water and drying on filter paper for 24 h at room temperature (similar to [9]).

Raman spectra were obtained using a Bruker Senterra 2 instrument equipped with a 532 nm laser. The laser power was 25 mW and a 50 μm aperture was used. An integration time of 5 s was applied with 5 co-additions. The stated spectral resolution was 4 cm⁻¹. Raman spectroscopy was performed on two sets of samples: the as-received YSZ-8 sample and the heated sample in dry, wet treated (straight after 30 vol% H2O2 treatment) and dry treated states.

The Raman spectra for the three states of the as-received material and the material treated for 1 week are shown in Fig. 2. Raman peaks for both the monoclinic and tetragonal phases of PtZ are consistent with previous studies [19,20,21] (and are highlighted in Fig. 2). There were no observed changes in the characteristic peaks between the samples, with both tetragonal and monoclinic peaks being discernible and analysis using the methodology of [21] indicating a tetragonal phase composition of 55%.

A large peak at 876 cm⁻¹ was observed in the wet, treated sample which is consistent with the O\textsuperscript{2−} ion stretching mode in hydrogen peroxide solution [22,23]. A peak remains at 840 cm⁻¹ in the dried sample that was not present in the original sample (a smaller peak in this position was also evident in the sample removed from H2O2 solution after 1 day). This 840 cm⁻¹ peak is consistent with the O−O peroxy ion stretching mode reported in previous work in MgO and Mg/BaO catalysis material reported by Lunsford et al. [11] as well as Su and Bell [12]. Additionally, the 840 cm⁻¹ peak is consistent with the peroxy ion observed in BeO using similar sample preparation techniques to those used in this study [24]. The peak at 840 cm⁻¹ was still evident after four weeks (stored at room temperature in a desiccator). The peak height had diminished to approximately half of the 24 h dried sample. The peak was not apparent after heat treatment of the sample at 200 °C for 2 h.

The YSZ-8 material that was heat treated to 1200 °C was analysed in a similar manner to the as-received material. Only tetragonal peaks were observed in the pre-treated sample. After treatment in the hydrogen peroxide solution, the peak at 876 cm⁻¹ was observed in the wet sample, but upon drying, no additional peaks were observed when compared to the pre-treated sample (indicating that the mode affiliated with the additional peak in the non-heat treated sample is associated with the monoclinic phase).

To further investigate the potential for peroxy ion formation in YSZ-8, DFT calculations were performed with the Vienna Ab-initio Simulation Package (VASP) [25–28]. The projector augmented wave (PAW) [29,30] library supplied with the software was used with a GGA exchange correlation functional described by Perdew, Burke and Ernzerhof [31,32]. The cut-off energy was set at 500 eV for all calculations with a Gaussian smearing width of 0.1 eV. The self-consistent field (SCF) stopping criterion was set to 1 × 10⁻⁶ eV and the geometry optimization stopping criterion was set at 1 × 10⁻⁶ eV.
and simulation cell vectors were all free to relax during energy minimisation unless stated. In all calculations, a gamma-centred 4 × 4 × 4 k-point grid was set automatically using the Monkhorst-Pack scheme. Monoclinic and tetragonal polymorphs of ZrO₂ doped with Y₂O₃ were considered – each with 32 cation sites and 64 oxygen sites. Two Y atoms were substituted onto two Zr sites in each supercell (producing a 6.25 mol% composition – a good comparison to the experimental material) and charge compensated through the formation of an oxygen vacancy in a ratio of 2:1 to maintain charge neutrality forming the \( {\left[ 2Y_{\text{Zr}}::V_{\text{O}}^{\cdot\cdot} \right]} \) cluster. The arrangement of the defect cluster is considered in a similar manner to previous studies [7,33,34].

The solution energy of Y₂O₃ into the monoclinic and tetragonal phases was first assessed in order to identify the lowest energy arrangement of the \( {\left[ 2Y_{\text{Zr}}::V_{\text{O}}^{\cdot\cdot} \right]} \) cluster in the tetragonal and monoclinic structures. The Y substitutional species were most stable when in a second nearest neighbour position towards the oxygen vacancy whilst being at a maximum separation from each-other, similar to previous atomic scale studies [7,35]. Solution of Y₂O₃ into monoclinic and tetragonal polymorphs is predicted to proceed with energies of 1.79 eV and 1.09 eV, respectively, via the following reaction (using Kröger-Vink notation [36]):

\[
Y_2O_3 + 22ZrO_2 + O_0^{\cdot\cdot} → 22ZrO_2 + 2Y_{\text{Zr}} + V_{\text{O}}^{\cdot\cdot}
\]  

(1)

This calculated reduction in solution enthalpy in forming a tetragonal phase highlights the stabilizing effect that substituting Y has in the ZrO₂ system.

Further calculations were performed to investigate accommodation of an extra oxygen atom into the Y-containing monoclinic and tetragonal polymorphs of ZrO₂. The additional oxygen was placed directly onto the charge balancing vacancy site. After relaxation, a configuration consistent with the peroxide ion defect formed through the lattice relaxation procedure. To gauge the propensity for oxygen to enter the monoclinic or tetragonal structures, solution was considered from molecular oxygen. The solution enthalpy was computed to be −0.03 eV and 0.79 eV in the monoclinic and tetragonal structures containing the \( {\left[ 2Y_{\text{Zr}}::V_{\text{O}}^{\cdot\cdot} \right]} \) defect cluster, respectively. The O—O bond distances associated with the defect were 1.49 Å and 1.48 Å in the monoclinic and tetragonal structures: consistent with the peroxide ion (\( O_{2}^{\cdot\cdot} \)) [37].

The near-zero solution enthalpy of O₂ into monoclinic ZrO₂ containing \( {\left[ 2Y_{\text{Zr}}::V_{\text{O}}^{\cdot\cdot} \right]} \), as well as the low energy computed for solution into the tetragonal structure indicates that the stoichiometry in the (ZrO₂)ₓ(Y₂O₃)₁₋ₓ system can vary, depending on the polymorph present and composition of the (ZrO₂)ₓ(Y₂O₃)₁₋ₓ. The preference for oxygen accommodation in the monoclinic phase echoes the experimental observation that the peak at 840 cm⁻¹ was only observed in the sample with a significant monoclinic phase fraction.

To calculate the vibrational wavenumber associated with the additional oxygen defect cluster (the neutral O₂ stretching) \( v(\text{O}−\text{O}) \), the cluster was compressed and stretched along its axis in increments of 1.25%. The spring constant was calculated by taking the derivative of the energy-distance function. The wavenumber was then determined from the spring constant via [9]:

\[
v = \left( \frac{k(2m)}{4\pi^2c^2m^2} \right)^{1/2}
\]  

(2)

where \( k \) is the spring constant in N/cm², \( m \) is the mass of an oxygen atom in kg, and \( c \) is the speed of light in cm/s. The wavenumbers associated with the O—O stretching mode, calculated in both the monoclinic and tetragonal structures, were 851 cm⁻¹ and 804 cm⁻¹, respectively. The extra peak observed in Fig. 2 at 840 cm⁻¹ is therefore consistent with extra oxygen being accommodated in the monoclinic PSZ structure through the formation of peroxide ions, that is, consistent with the experimental observation indicating the presence of the monoclinic polymorph and the modelling prediction indicating the significant preference for excess oxygen to reside within the monoclinic polymorph.

To conclude: we have demonstrated through a combination of experiment and modelling methods that the accommodation of excess oxygen beyond the standard \( (ZrO_2)_{(2Y_{\text{Zr}})}(Y_{\text{O}})_{(1)} \) is plausible. The preferable enthalpy of solution suggests that the solubility of oxygen in the monoclinic structure is favourable, whilst solubility of oxygen into the tetragonal polymorph may proceed only once entropic factors are considered – both oxides forming the O₂⁻ peroxide defect, supported by Raman spectra in this work. The Raman active stretching mode of this defect was predicted and shown consistent with experimental observations of the YSZ-8 which highlighted the formation of a new peak upon treatment in 30% H₂O₂ solution. Further work to corroborate this prediction could include NMR spectroscopy, carried out with oxygen-18 H₂O₂ solution and alternative oxidation routes. The impact of deviation in stoichiometry on the ionic conductivity in this material is of particular interest when considering its long-term efficiency and behaviour for fuel cell and related applications (it is not known whether the presence of the defect will aid or hinder ionic conductivity). The results may also play an interesting role in the mechanical degradation of yttria-doped zirconias, potentially stabilizing or accelerating the formation of the monoclinic phase (e.g. during so-called low temperature degradation LTD [19]).

**Acknowledgements**

This work was carried out as part of the Sêr Cymru II programme funded through the Welsh European Funding Office (WECF) under the European Development Fund (ERDF). Computing resources were made available by HPC Wales and Supercomputing Wales. SCM would like to acknowledge the support of the members of the MÚZIC-3 programme, particularly Magnus Limbäck, Antoine Claisse and Jonna Partezana.

**References**