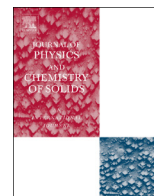




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## Journal of Physics and Chemistry of Solids

journal homepage: [www.elsevier.com/locate/jpcs](http://www.elsevier.com/locate/jpcs)

## Investigation of the vibrational properties of cubic yttria-stabilized zirconia: A combined experimental and theoretical study

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## ARTICLE INFO

## Article history:

Received 15 August 2013

Received in revised form

28 October 2013

Accepted 31 October 2013

Available online 8 November 2013

## Keywords:

A. Oxides

C. ab initio calculations

C. Neutron scattering

D. Phonons

## ABSTRACT

A combined experimental and theoretical investigation into the vibrational properties of cubic 8–9 mol% yttria-stabilized zirconia (YSZ) is presented. Measurements of acoustic phonon dispersion curves have been obtained from inelastic neutron scattering investigations using a triple axis spectrometer, as well as calculations of the vibrational density-of-states (vDOS) using density-functional theory. The present measurements agree closely with, and extend, previously published results. The phonons become broader and decrease in intensity as the Brillouin zone boundary is approached, particularly in the  $\Gamma$ - $\Delta$ - $X$  direction. Interestingly, there is evidence of a previously unreported low energy phonon band (8–9 meV) in the  $\Gamma$ - $\Sigma$ - $X$  direction, which could possibly be related to the stabilization (by yttria doping) of the imaginary mode of cubic  $ZrO_2$  about the  $X$ -point. Compared to pure cubic  $ZrO_2$ , the vDOS of YSZ are broader and extend to higher frequency. Furthermore, the prominent Zr-related feature in the vDOS of  $c$ - $ZrO_2$  at  $\approx 14$  meV is shifted to higher energy in the vDOS of YSZ. This behavior is consistent with the measured dispersion bands (first acoustic branch in the  $\Gamma$ - $X$  direction, about the  $X$ -point) of YSZ which is higher in energy by a similar amount relative to that of  $c$ - $ZrO_2$ , thus providing support for the structural model considered.

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## 1. Introduction

Zirconium oxide ( $ZrO_2$ ) or zirconia, has a large range of materials applications because of its high strength and stability at elevated temperatures. Zirconia can be used as a structural ceramic and is an important component in catalytic converters, oxygen sensors, and in chemically passivating surfaces. It is one of the best corrosion-resistant and refractive materials used in metallurgy, and is also utilized as a thermal barrier coating in engines [1–3]. Zirconia is one of the most radiation resistant ceramics currently known, and is of particular interest to the nuclear industry where it has been used, for example, as a passivating medium for hydrogen ingress in pressure tubes [4–6]. The structural and electronic properties of zirconia have been widely reported (e.g. Refs. [7–9]). Zirconia is an insulator, which forms in three temperature dependent polymorphs: Monoclinic zirconia

( $m$ - $ZrO_2$ ) at ambient conditions [10], tetragonal ( $t$ - $ZrO_2$ ) at about 1440 K [11], and cubic fluorite ( $c$ - $ZrO_2$ ) at around 2640 K [12]. A melt forms at temperatures of about 2950 K.

The addition of yttria ( $Y_2O_3$ ) to zirconia results in the ceramic material known as yttria-stabilized zirconia (YSZ) [3]. At ambient temperature and pressure, YSZ can form in a tetragonal phase (for a concentration of 2–9 mol% yttria) and a cubic phase (4–40 mol% yttria). Below 4 mol%, monoclinic  $ZrO_2$  is present. A rhombohedral “ $\delta$ -phase” forms for yttria concentrations above 40 mol% [13–15]. The yttrium (3+) cations are aliovalent to the zirconium (4+) cations and this necessitates the inclusion of oxygen vacancies into the lattice, so that charge neutrality is maintained [16]. Yttria stabilized zirconia has applications as ion conductors in solid oxide fuel cells, as oxygen sensors and in various catalysts [17,18]. It is also used as thermal barrier coatings (TBC), e.g. for gas turbines [19]. Cubic-stabilized-zirconia has furthermore been proposed as part of the inert fuel matrix in nuclear reactors [20].

The atomic structure of YSZ has been the subject of much past and current research [21–23]. Morell et al. [24] investigated the Raman spectra of cubic YSZ containing 9.5 mol%  $Y_2O_3$ . Spectral analyses of phonon density-of-states indicated results consistent

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with a non-random arrangement of oxygen vacancies. Goff et al. [25] studied YSZ with 9.4–24 mol%  $Y_2O_3$ , and reported that vacancies are found in single-vacancy, divacancy or aggregated di-vacancy clusters, depending on the degree of doping. Further, this work proposed that oxygen vacancies occur in vacancy-zirconium-vacancy units that are separated along the  $\langle 112 \rangle$  direction. In a study of cubic YSZ for 9.5–24 mol%  $Y_2O_3$ , Argyriou et al. [26], using neutron diffraction, found among other things that the O-atom is predominantly displaced in the  $\langle 100 \rangle$  direction and to a lesser extent in the  $\langle 111 \rangle$  direction, and also that appreciable amounts remain at the ideal fluorite sites. From extended X-ray absorption fine structure (EXAFS) studies of the local structure, it was reported that oxygen vacancies are situated as first neighbors to Zr atoms and Y atoms are 8-fold coordinated [27].

Theoretically, the atomic structure of YSZ has attracted considerable attention, with progress being made on the basis of first-principles density-functional theory (DFT) calculations [28–32]. The results of these theoretical investigations largely support the interpretation of experimental results and show that the structure formed is dependent on the percentage of yttria included [28,29,31–33]. In particular, Bogicevic et al. [28] carried out extensive first-principles investigations and established a number of constraints that the atomic structure of YSZ would follow, related to the stable  $\delta$ -form of YSZ.

Defects in a crystal structure are well known to potentially induce localized phonon modes, and alter the vibrational density-of-states (vDOS) and the lattice heat capacity. Therefore, studies into the vDOS can give information about the local defect structures (e.g. O vacancies, or Y substituting Zr). An understanding of the lattice dynamics is also of interest with regards to the material's ion conduction properties, and also with regard to any technologically important phase transformations. An early work by Liu et al. [34], using inelastic-neutron-scattering, investigated the frequencies and linewidths along the three principle symmetry directions of cubic YSZ with 20 wt%  $Y_2O_3$ , for temperatures up to 1700 K. Longitudinal acoustic (LA) and transverse acoustic (TA) phonons were observed, but not optical-phonon branches, consistent with earlier Raman scattering data. This work also reported that acoustic phonons rapidly broaden in the three high-symmetry directions. In a later study by Argyriou and Elcombe [35], the acoustic phonon dispersion curves were measured for three cubic stabilized zirconias (9.5 and 24 mol%  $Y_2O_3$ , and 12.5 mol% CaO) at room temperature using a triple axis neutron spectrometer. Similarly to Liu et al. [34], LA and TA branches were observed, but optical phonons were not reported.

With regard to theoretical investigations of the vibrational properties and lattice dynamics for  $ZrO_2$ , such properties have been studied in detail, as well as the various phase transformations (see e.g. Refs. [36–46]). For cubic YSZ, there have only been a few studies, which are briefly described below.

Tojo et al. [47] investigated the thermodynamic properties using molecular dynamics simulations with interatomic potentials, for 8, 10, 12 and 14 mol%  $Y_2O_3$  doped  $ZrO_2$ . The calculated heat capacity was found to be a maximum at 10 mol%, which coincides with experimental results. Tojo et al. [47] also calculated the total and partial phonon density-of-states of YSZ for 8 mol%  $Y_2O_3$ . These results showed additional vibrational modes compared to  $ZrO_2$  at low frequencies, caused by structural defects in the crystal. In another theoretical study, Shelling et al. [48] performed classical molecular-dynamics simulations of the temperature dependence of the thermal conductivity of  $ZrO_2$  and YSZ, for a range of concentrations. They also reported the density of local frequencies for 4 and 20 mol% yttria YSZ, finding that the disorder in the oxygen local frequencies is increased, but the range of the distributions is largely unchanged. Ostanin et al. [16,49] performed first-principles theoretical investigations of YSZ between 3 and

10 mol%  $Y_2O_3$  using density-functional theory (DFT) and the pseudopotential approach. They calculated the vibrational mode corresponding to the zone-boundary soft phonon,  $X_2^-$ , of cubic  $ZrO_2$ , for YSZ between 3 and 10 mol%  $Y_2O_3$ , where the results showed a phase transition to cubic YSZ at 10 mol%  $Y_2O_3$ .

Lau and Dunlap [50] used DFT calculations to investigate the dielectric, thermodynamic and phonon properties of YSZ structures, predicted from previous calculations of ground state structures [31], having 14, 17, 20, and 40% mol  $Y_2O_3$ . Regarding the phonons studied, they report the total phonon density-of-states for the so-called  $\delta$ -phase of YSZ for 40 mol%  $Y_2O_3$ , but not for lower concentrations. In the work of Dalach et al. [32], using a cluster expansion and a statistical thermodynamics approach based on DFT results, among other findings, they predicted the atomic ordering as a function of dopant concentration, where it was found that below 9 mol%  $Y_2O_3$ , cation dopants show a tendency to aggregate. Regarding total phonon density-of-states, results were presented for 33 and 66 mol%  $Y_2O_3$ , in which it was shown that cations are primarily responsible for low-frequency modes at 5–6 THz (21–25 meV), mixed cation–anion participation for 7–15 THz (29–62 meV), and high frequency modes primarily resulting from anion vibrations at 15–23 THz (62–95 meV).

In the present paper we perform inelastic neutron scattering experiments for YSZ with 8–9 mol%  $Y_2O_3$  and discuss the results in relation to phonon density-of-states calculated using DFT, for two model atomic structures based on predictions from extensive *ab initio* investigations of ground state structures [28]. One of these structures contains a long-range structural motif (O-vacancy–Zr–O-vacancy) oriented along the  $\langle 112 \rangle$  direction, a configuration considered based on the findings of Goff et al. [25]. This structural model has also been used in first-principles calculations in which the Kohn–Sham eigenvalues are compared with core-level binding energies measured by X-ray photoelectron spectroscopy (XPS) [51]. To the best of our knowledge, calculated first-principles total and partial phonon density-of-states for this concentration of YSZ and comparison with experiment, have not been presented to date. The paper is organized as follows: In Section 2, the experimental procedure and results are described, followed in Section 3 by the theoretical method and results. Section 4 contains the conclusions.

## 2. Experiment

The Taipan thermal triple-axis spectrometer (TAS) [53] at the OPAL reactor [52] located in Sydney, Australia, was used to map phonon dispersion for YSZ(100) with 8–9 mol%  $Y_2O_3$ . TAIPAN is similar in concept to triple-axis spectrometers IN8 [at the Institut Laue-Langevin (ILL)] and PUMA [Research Neutron Source, Heinz Maier-Leibnitz (FRM-II)] that allow variable incident and final energies, and have a secondary spectrometer with a single detector [54]. The location of TAIPAN is on a tangential thermal neutron beam tube at the OPAL reactor shielded face. For these experiments TAIPAN uses the (002) planes of a highly oriented pyrolytic graphite (HOPG) as the double-focusing monochromator and analyzer. For TAIPAN, the secondary spectrometer consists of separate sample, analyzer and detector stages, which are mounted on air pads that move on a polished granite floor. The secondary spectrometer is conventional and has polyethylene shielding installed around the analyzer and detector elements. The incident energy range of TAIPAN TAS is from  $\approx 5$  meV to  $\approx 80$  meV. There is a monitor positioned downstream from the monochromator that counts the number of neutrons in the incident beam and is used as a gate to dose the same number of neutrons incident on the sample for each  $E_n(Q)$  point measured. Instrument control and

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