Available online at www.sciencedirect.com
ScienceDirect
Physica B 389 (2007) 116–119
PHYSICA B
www.elsevier.com/locate/physb

Ab-initio study of the hyperfine parameters in $P2_1/c$, P42nmc and Fm3m zirconia phases doped with Ta_{zr} and the vacancy–Ta_{zr} complex

R.A. Casali[a,*], M.A. Caravaca[b]

[a]*Facultad de Ciencias Exactas, y Nat. y Agr.-UNNE-Avenue Libertad 5600, Corrientes, Argentina*
[b]*Facultad de Ingeniería-UNNE, Avenue Las Heras 727, Resistencia, Argentina*

Abstract

In this work we develop selfconsistent calculations by means of the all-electron method NFP-LMTO. The electronic structure, quadrupolar frequencies and asymmetry parameters of ZrO_2 polymorphs doped with Ta placed at substitutional site to Zr (Ta_{Zr}), with and without vacancies are studied in the monoclinic, tetragonal and cubic phases. The calculated hyperfine parameters in neutral Ta_{Zr} in the monoclinic phase are in agreement with hypine parameters measured with PAC and assigned to substitutional site in a wide range of temperatures. However, in the case of Ta_{Zr} in the tetragonal P42nmc phase, the electric field gradient (EFG) is in large disagreement with the experimental assignment. Therefore we explored the incorporation of a near neighbor oxygen vacancy in several charged states. We found that the TaV^0 and TaV^{+1} pairs in the tetragonal symmetry with axis length ratio $c/a = 1.02$ gives electric field gradients V_{zz} and η in agreement with low-temperature values of the experimentally assigned pure tetragonal, called *t*-form. Further, the pair Ta-V with a ratio $c/a = 1$ gives EFG in close agreement with reported high-temperature values.

PACS: 61.72.Ky; 71.20.Ps

Keywords: Oxides; Hyperfine interactions; Ab-initio calculations

1. Introduction

Zirconia is considered the more important ceramic, after alumina. This and other oxides with the metal ion atom belonging to the group IV, are candidates for several technological applications such as fast-ionic conductor of oxygen, for example. For them, the properties of the defects, in particular the oxygen vacancies are very important and have been investigated abundantly during the last decades. The stable structure in bulk, undoped ZrO_2, is monoclinic. The addition of a trivalent metal oxide, as yttria (Y_2O_3), partially stabilizes the tetragonal structure in ZrO_2–2.8 mol%Y_2O_3 solutions and fully stabilizes the cubic structure for ZrO_2–11 mol%Y_2O_3 solutions. The obtained material is characterized by its high fracture toughness and abundant vacancy lattice sites (one for every two yttrium atoms added), which provide a proper pathway for oxygen conduction. Nanopowders made of pure ZrO_2 with grain size below 60 nm also stabilize the tetragonal structure, and down below to 2 nm, the cubic one, in a mechanism that today is not completely understood.

Electric quadrupolar interactions operate in the solid at nanometric scales. Therefore, they are particularly appropriate for nanoparticle study. The hyperfine parameters at the Ta probe site in the monoclinic ($P2_1/c$) and tetragonal (P42nmc) bulk phases of zirconia are experimentally known [1,2]. By comparison it was tempting to identify the interactions observed in nanocrystals of the same compound [3–5]. A number of investigations in pure ZrO_2 [3], 2.8% yttria partially stabilized ZrO_2 [4] and 11.3% yttria-stabilized ZrO_2 [5] oxides obtained by the sol–gel method, focused the attention on the preparation parameters of the starting solution on some features of zirconia powders, i.e.: the morphology, polymorphic phase content, and involved nanostructures, and also the thermal transformations and crystallite size evolution. In these

*Corresponding author. Tel.: +54 3783 473931; fax: +54 3783 473930.
E-mail address: rac@exa.unne.edu.ar (R.A. Casali).

0921-4526/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2006.07.036

investigations [3–5], several sol–gel-derived zirconias resulting from precursor solutions of different pHs and their thermal evolution were studied by using the highly localized perturbed angular correlation (PAC) spectroscopy, the complementary bulk techniques of X-ray diffraction (XRD), differential thermal analysis–thermogravimetric analysis (DTA–TGA), and specific surface area measurements (for instance nitrogen adsorption Brunauer–Emmett–Teller (BET) method) [3–5].

The dominant contribution to the PAC spectra is characterized by an electric field gradient (EFG) with a quadrupolar frequency of ω_Q of 160 Mrad/s at 400 °C, which drops to 120 Mrad/s at 1000 °C [3]. This interaction was assigned to Ta in the t′ phase (distorted tetragonal nanostructure), has an asymmetry parameter $\eta = 0.6$ and a large distribution. This suggests that the places of Zr have a highly disordered environment, added to a distribution of probe sites located at the crystalline interfaces. The other two PAC components correspond to ZrO_2 in monoclinic (m phase) form, with hyperfine parameters almost constant (120 Mrad/s and $\eta = 0.4$) for a wide range of temperatures, and the site named t-form, assigned to the eight oxygen-coordinated, slightly distorted (180 Mrad/s at 400 °C, 160 Mrad/s at 1000 °C, $\eta = 0.2$–0) configuration [3]. This last one is a quite-ordered nanostructure that predominates at higher temperatures and exhibits a crystalline (assigned in the literature) tetragonal pattern at all temperatures. In most zirconias prepared by the sol–gel method starting from an organic precursor, in addition to the previously described tetragonal t′-form, part of the as-obtained amorphous product as revealed in XRD is described by another very disordered configuration with $\omega_Q = 200$ Mrad/s and $\eta = 0.55$ [3], named x-form. Very recently, the nuclear spectroscopy PAC was used to investigate another complex, the t″-form and the t″-c transformation in ZrO_2–10%Y_2O_3 nanopowders synthesized with nitrate–citrate gel combustion process combustion method [6]. These powders are used as electrolyte in solid oxide fuel cells (SOFCs). The t″-form is called pseudocubic because of its $c/a = 1$, but with oxygen displacements lower than that assigned to the t′-form and hardly distinguishable form the fluorite type. While the t-form posseses a c/a close to 1.015, in the t′-form c/a is close to 1.007 [6]. In close connection to the present work, very recently, we studied theoretically Ta-doped HfO_2 polymorphs free of vacancies. We have found that the EFGs depend strongly on the phase and the charge state of the Ta impurity. Also, a surprisingly low EFG for the tetragonal phase (P42nmc) was found in that work, which contradict the experimental assignment of the t-form. Because of the different coordination and restructurations of the neighborhood around the probe atom, according to the phase ($P2_1/c$, Pnma, Pbca, Fm3m, or P42nmc) where it resides [8], the calculated hyperfine parameters were very well distinguished from other. Therefore, the main conclusion was that the calculations can be utilized with PAC to identify phase transitions upon temperature and (possibly) under pressure.

It is the aim of this work to study theoretically the EFG in pure–Ta-doped phases: $P2_1/c$ (monoclinic), P42nmc (tetragonal) and the Fm3m (cubic) under the influence of near vacancies to the Ta atom. Applying uniaxial deformations we mimic the influence of the coexistence of grains of different symmetry, as the monoclinic and tetragonal. Varying the charge states of Ta and the complex Ta–V, we try to reproduce the real conditions of the impurities in the material, due to the presence of co-dopants or electrons provided by grain boundaries, for instance.

2. Theoretical approximation

Bulk system defect has been simulated by means of the supercell technique that consists of a periodic repetition of cells with tetragonal, monoclinic or cubic symmetries containing 48 atoms of ZrO_2, or more, precisely $Zr_{16}O_{32}$. For the EFG calculations, a Ta impurity is included (Ta_{Zr}) substituting a Zr atom, resulting in the formula $Zr_{15}O_{32}TaZr$. To simulate the presence of yttrium atoms in the solution as well as the formation of possible oxygen selfinterstitial-vacancy pairs upon temperature, an oxygen vacancy (V_O) is included as a nearest neighbor to Ta, we obtain the formula $Zr_{15}O_{31}TaZrV_O$. In the 48-atom cell, this corresponds to a 2.1% concentration of dopant impurities. Neither the presence of yttrium nor the oxygen selfinterstitial, are included in the present formulation. Since the extraction of an oxygen atom gives rise to a (+2) vacancy, this charged defect is partially compensated by the electron in excess provided by the Ta atom, obtaining finally a +1-charged center. We assume that the pair can exchange electrons with the environment, so the system was studied with 0-, +1- and +2-charged states. In this way, the supercell is more accurately expressed by the formula $Zr_{15}O_{31}TaZrV_O^q$, where V_O represents an oxygen vacancy and q the complex charged state. The incorporation of a charge state in the supercell was simulated by diminishing (in our case, $q>0$) the number of electrons in the electronic structure in multiple of one electron. In order to maintain the cell electric neutrality, an opposite amount of charge ($-q$) is added to the supercell electrostatic background.

The ab-initio all-electron new-full-potential linear-muffin-tin-orbitals (NFP-LMTO) [9,10] method is based on smooth Hankel functions. Our code uses the density-functional theory in the local approach (LDFT) to account for the many-body electronic interaction. The delocalized valence states in our selfconsistent calculation are provided by: $4d^2$, $5s^2$ and $5p^0$ for Zr, $5d^3$, $6s^2$ and $6p^0$ for Ta and $2s^2$, $2p^4$ for oxygen. The wave functions basis set are here constructed with s, p, d blocks, for the Zr atom, s, p, d, f blocks for Ta and s, p, d blocks for the O atom. The smooth ratio and the decay of each block were optimized individually in the fluorite phase to obtain total energies converged to a few mRy/atom. In the present implementation of the FP-LMTO, the wave functions are represented