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Orthorhombic phase stabilization and transformation phase process in zirconia tantalum-doped powders and spark plasma sintering systems

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ABSTRACT

The role of different amount (from 1 to 20 mol%) of tantalum Ta(V) into the zirconia lattice has been investigated in different powders systems prepared *via* co-precipitation and after calcination. The X-ray diffraction and Raman analyses, have confirmed the presence of an orthorhombic phase in all the samples. The stability of this phase has been investigated by "in situ" X-ray diffraction analysis from 100 °C to 1000 °C and after the subsequent cooling. A phase transformation mechanism, with the formation of a poor (monoclinic) and a rich phase (orthorhombic) in Ta has been consider in order to explain the XRD patterns obtained at different temperatures. The characterization of the orthorhombic phase on bulk ceramic specimens prepared via Spark Plasma Sintering (SPS) has been also investigated. SEM analysis has confirmed the presence of a two-phase system.

1. Introduction

Zirconium oxide or zirconia (ZrO_2) is an interesting and useful metal-oxide. Many different applications fields are involved on zirconia-based materials research, thanks to its good mechanical, thermal, functional and sometimes unique properties [1,2]. Common uses for these ceramic materials are thermal barrier coatings (TBCs) [3], dental and bone prostheses [4,5], high resistance laminates [6–9], solid oxide fuel cells (SOFCs) [10,11], gas sensors [12–14] and optical devices [15,16], catalysis and luminescent materials [17–19] and new nanoparticles (NPs) [20–23].

The technological importance of zirconia as structural material is related to the tetragonal-to-monoclinic martensitic transition. Yttria-stabilized zirconia is the most used doped system since having superior mechanical properties [1]. The tetragonal phase, partially or fully stabilized, can be prepared doping with a controlled percentage of Y^{3+}, but also other cations such as Mg^{2+}, Ca^{2+} and Ce^{4+} have been employed as stabilizing ions. Zirconium is a tetravalent cation, so charge compensation is necessary when a trivalent or bivalent cation is introduced into the zirconia crystalline structure. Due to such compensation, oxygen vacancies are formed as amply described in literature [2]. These vacancies seem to stabilize the tetragonal zirconia ceramics compounds. However, this stabilization is also the source of two mean cracking process due to a retransformation to a monoclinic phase with larger volume: transformation toughening and low temperature degradation (LTD) [4,24,25]. This is an important drawback: aging and moisture could determine unexpected (brittle) cracking in zirconia ceramic devices. Therefore, in the last years, the limitations of partially tetragonal stabilized zirconia in engineering and medical applications have been thoroughly discussed [24,26–29].

As a possible solution, since the oxygen vacancies are induced by trivalent (or bivalent) cations, pentavalent doping cations (Ta^{5+}, V^{5+} and Nb^{5+}) have been used to prevent this type of defect [30,31]. The possibility to prepare a stable vacancies-free zirconia ceramic with good mechanical properties represents an excellent approach in order to refresh the appeal of zirconia as a structural material. Some technological advantages have been already reported in

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literature such as a better hot corrosion resistance for TBCs [31–34] concerning zirconia tantalum-doped materials.

In parallel to the research of new ZrO_2 based systems with enhanced macroscopic properties, some papers have evidenced the presence of three orthorhombic phases into zirconia systems, stabilized also by some dopant such as MgO, at high pressure and temperature. For some of these systems, with specific composition, detailed structural studies have been reported [35–38 and reference therein]. In particular, pure zirconia system shows Pbca (3.5–15 GPa) and Pnam (over 15 GPa) orthorhombic phases stable at high-pressure [36]. Moreover, different doped and co-doped zirconia systems with Ca or Mg [39], or some alloy systems evidence the $Pbc2_1$ (an allowed transformation of the $Pca2_1$ space group) orthorhombic phase as reported by Kisi et al. [36]. Even though zirconia Ta-doped systems have been previously studied, very scarce and not always coherent data are available on phase analysis [30,33,40–43]. The homogeneity range of orthorhombic phase was found to be up to 33 mol% of Ta_2O_5 in ZrO_2 [44]. In particular, on samples with low Ta content, some paper reports that the addition of Ta brings about the gradual stabilization of the tetragonal ZrO_2, meanwhile, some others show the presence of an orthorhombic phase. Probably, since the differences between the two phases are particularly evident at angles higher than 35° in 2θ, the X-ray diffraction results have been variously interpreted due to the too limited range of the patterns investigated [45]. Recently, we have reported a detailed X-Ray diffraction analysis on a ZrO_2 sample doped with 16 mol% of $TaO_{2.5}$ [46] and we have identified the high pressure $Pca2_1$ orthorhombic structure reported by Kisi et al. [36] as the main crystalline phase.

Despite the extensive Raman knowledge of the well-known zirconia polymorphs (i.e. monoclinic, tetragonal and cubic) the orthorhombic phase, in all his forms (Pnam, Pbca, $Pca2_1$) has not been investigate in details. The only system published, in which both calculated vibrations and experimental data match, concerns the orthorhombic Pnam system, which identifies the cotunnite-type phase [48,49]. Generally, other attempts, performed to discriminate the orthorhombic Pbca, cannot be considered fully reliable. The main difficulty arises from the restricted number of high pressure-induced polymorphs, transformed from either monoclinic [50,51] or tetragonal [52] zirconia, studied so far. Different pressure-annealing treatments involves different grade of lattice distortions, leading to different crystallographic systems and consequently different Raman mode shifts.

Aim of the paper is to investigate the role of Ta as a dopant agent, in a specific range of composition into the ZrO_2 structure as stabilizer of the orthorhombic phase in the powder and in the consolidated specimens. In detail, the study was carried out as follows: a) Seven ZrO_2-$TaO_{2.5}$ doped powdered systems, with the amount of Ta ranging from 1 to 20 mol% of $TaO_{2.5}$ (ZT1, ZT3, ZT4, ZT5, ZT8, ZT12, ZT20), were prepared by a catalyzed co-precipitation route; b) the thermal evolution and the stabilization of the crystalline phases were analyzed "in situ" and "ex situ" by XRD patterns using also a synchrotron line; c) a detailed Raman spectroscopy analysis was performed; d) the three more significant powdered systems were consolidated *via* Spark Plasma Sintering (SPS) at two different temperatures and pressures; e) a detailed XRD and SEM analysis of the consolidate systems were conducted to define the role of Ta in the final microstructure.

The present study have also showed that the lower limit relative to the stabilization of the orthorhombic phase, in the system ZrO_2-$TaO_{2.5}$, is 16 mol% instead of 25 mol% of $TaO_{2.5}$ as reported in literature [31,34,43,47]. The XRD analysis of the two systems show that the same orthorhombic phase ($Pca2_1$) had to be used to describe both the crystalline structures.

2. Material and methods

2.1. Materials

Zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$; Aldrich 98%), tantalum(V) chloride anhydrous ($TaCl_5$; Aldrich 99.8%), ammonium hydroxide (NH_4OH; Fluka 28 wt%), ethanol (EtOH; Aldrich 99.8%), and distilled water. All reagents were used as received without further purification.

2.2. Synthesis of the powders

Ta-doped ZrO_2 powders were prepared via the base catalyzed coprecipitation method, already used for other similar works [21]. Briefly, ethanolic solutions 0.1 M $ZrOCl_2{\cdot}8H_2O$ and 12.5 mM $TaCl_5$ were mixed together in different amounts while stirring at ambient temperature. Co-precipitation to the corresponding hydroxides was achieved by drop-wise addition of excess aqueous ammonia. After 20 min of stirring at room temperature, the co-precipitated hydroxides were centrifuged (9000 rpm for 30 min) and washed once with distilled water and three times with EtOH to remove excess ammonia and unreacted precursors, then dried at 130 °C for 12 h. The as-obtained powders were calcined in air at 1000 °C for 6 h to promote the crystallization and transformation to the mixed oxides.

2.3. Powder consolidation

The consolidation process of the zirconia Ta-doped powders (ZT5, ZT8, ZT12) via Spark Plasma Sintering (SPS) has been performed with a Dr. Sinter Lab SPS 515S equipment at two different experimental conditions sets: a) T = 1250 °C, P = 75 MPa, t = 5 min (SPS1250 series), b) T = 1150 °C, P = 100 MPa, t = 5 min (SPS1150 series). Lower sintering temperature needs higher sintering pressure in order to reach a good final density of the specimen.

2.4. Characterization

The microstructure of the powders was studied by means of X-ray powder diffraction (XRPD). A Philips diffractometer with a PW 1319 goniometer (Almelo, The Netherlands) with Bragg–Brentano geometry, connected to a highly stabilized generator (40 kV), was used for the preliminary XRPD measurements. A Bruker D8I-90 with Bragg–Brentano geometry, connected to a highly stabilized generator (40 kV), was used for the Wide-Angle X-Ray Scattering (WAXS) measurements of the sintered specimens. The "in situ" temperature XRPD measurements were collected at the ELETTRA Laboratories of Sincrotrone Trieste S.C.p.A (Line MCX) using a quartz glass capillary as sample holder [53]. The patterns were acquired in the range 100–1000 °C every 100 °C with a temperature ramp of about 0.17 °C/sec. Before any measurements, the temperature of the samples was kept constant for 10 min.

Grain size distribution, compositional Energy Dispersive X-ray Spectroscopy (EDS) analyses, Backscattered Electrons (BSE) and Secondary Electrons (SE) images on the sintered specimens have been preformed with a Zeiss Sigma VP FE-SEM c/o the Centro di Microscopia "Giovanni Stevanato" in Venezia-Mestre (VE, Italy). In order to evidence the grain boundaries the surfaces have been polished (lapping with diamond paste till 1 μm) and then have been annealed at one hundred degree lower respect to the SPS temperature.

Raman spectra were acquired with using a confocal (optical) microprobe from different areas of the samples. All Raman spectra were collected at room temperature using a single monochromator (T-64000, Jobin-Ivon/Horiba Group, Kyoto, Japan) equipped with a nitrogen-cooled 1024 × 256 pixels CCD camera (CCD–3500 V,

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