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Ceramics of Ta-doping stabilized orthorhombic ZrO_2 densified by spark plasma sintering and the effect of post-annealing in air

Gabriele Sponchia [a], Bibi Malmal Moshtaghioun [b], Alvise Benedetti [a], Pietro Riello [a], Diego Gómez-García [b,c], Arturo Domínguez-Rodríguez [b], Angel L. Ortiz [d,*]

[a] Department of Molecular Science and Nanosystems, Ca' Foscari Università di Venezia, via Torino 155/B, Venezia-Mestre I-30172, Italy
[b] Department of Condensed Matter Physics, University of Seville, 41012 Seville, Spain
[c] Institute of Materials Science in Seville, CSIC-US, Av. Americo Vespucio 49, Seville, Spain
[d] Department of Mechanical, Energy and Materials Engineering, University of Extremadura, 06006 Badajoz, Spain

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ABSTRACT

16 mol% Ta-doped ZrO_2 powders were synthesized and densified by spark-plasma sintering (SPS) in vacuum, followed by post-SPS annealing in air, thus obtaining two ultrafine-grained ceramics consisting of Ta-doping stabilized orthorhombic ZrO_2. The as-SPSed ceramic is black because it is actually a suboxide essentially with reduced cations and abundant oxygen vacancies, whereas the post-annealed ceramic is white because it is an oxide without vacancies and with only partially reduced cations. Both ceramics are relatively hard and brittle, but the as-SPSed ceramic was slightly more so, attributable to crystallographic and microstructural differences. Implications of interest for the ceramics community are discussed.

ZrO_2 is one of the most interesting, useful, and versatile engineering ceramics available today. This is because it finds applications in many different fields thanks to its good mechanical, thermal, and functional properties [1,2]. For example, some of the common uses of ZrO_2-based ceramics are as thermal barrier coatings (TBCs) [3], dental and bone prostheses [4,5], high-resistance laminates [6], solid oxide fuel cells (SOFCs) [7–9], gas sensors [10–12], optical devices [13,14], and in catalysis [15–17] and luminescent materials [18–20].

ZrO_2's great potential as a structural ceramic stems from the metastable retention at room temperature of its tetragonal polymorph, which, under the application of stress, transforms to the monoclinic polymorph. The volume expansion accompanying this transformation makes ZrO_2-based ceramics very tough, a phenomenon known as transformation toughening. Retention of the tetragonal polymorph is achieved by partially alloying ZrO_2 with other oxides, generally consisting of bivalent or trivalent cations because they substitute for Zr^{4+} cations in the crystal lattice, thus necessarily generating the oxygen vacancies [2] that metastabilize the tetragonal polymorph. Typical examples of such "stabilizers" are CaO, MgO, Y_2O_3, and a long list of rare-earth oxides, with Y_2O_3 being the most prominent [1]. Unfortunately however the metastability of the tetragonal polymorph also has important drawbacks in practice since its great susceptibility to aging and moisture [21,22] eventually leads to the premature catastrophic failure of the corresponding components in service. Consequently, there is currently growing concern about the long-term performance of tetragonal ZrO_2 ceramics in certain engineering applications, and particularly in the medical field.

A possible solution preventing this metastability could be substitutional doping with pentavalent cations [23,24] instead of with the commoner bivalent and trivalent cations. Developing stable, non-monoclinic, ZrO_2-based ceramics is technologically and scientifically interesting. Technologically, it could help to solve some of the current limitations of ZrO_2 ceramics in engineering applications. In this context it has been demonstrated for example that Ta-doped ZrO_2 ceramics possess improved hot-corrosion resistance for use as TBCs [24–27]. Scientifically, there is a need for systematic studies on crystallographic aspects and phase relations in systems containing ZrO_2 plus Me_2O_5. For example, Ta-doped ZrO_2 has been investigated before [23,26,28–32], but with controversial conclusions. It seems that Ta-doping can stabilize the orthorhombic ZrO_2 polymorph, but such aspects as homogeneity range, solubility limit, and space group, to name just a few, require further clarification. Also, it would be convenient to demonstrate the feasibility of processing these novel ceramics by spark-plasma sintering (SPS), which is increasingly being used for the ultrafast densification of other advanced ceramics. This is indeed the objective of this study, which was aimed at fabricating by SPS novel Ta-doping stabilized orthorhombic ZrO_2 ceramics, as well as at elucidating the effect of post-SPS

* Corresponding author.
E-mail address: alortiz@unex.es (A.L. Ortiz).

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annealing in air on both the microstructure and mechanical properties of the resulting ceramics.

16 mol% Ta-doped ZrO_2 powders were then synthesized by the base catalysed co-precipitation method [19,33], using 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 as starting materials. Briefly, two ethanolic solutions, one of 0.1 M $ZrOCl_2 \cdot 8H_2O$ and the other of 12.5 mM $TaCl_5$, were mixed together (42 mL plus 192 mL, respectively) while stirring at ambient temperature. Co-precipitation to the corresponding hydroxides was achieved by drop-wise addition of excess aqueous ammonia (3.1 mL). After 20 min of stirring, the co-precipitated hydroxides were centrifuged (9000 rpm for 30 min), washed once with distilled water and thrice with EtOH, then dried at 130 °C for 12 h, and finally crushed but not calcined.

Fig. 1 shows a photographic image of the two Ta-doped ZrO_2 ceramics (semi-discs) prepared from these powders, both by SPS (Dr. Sinter SPS-515S, Sumitomo Coal Mining Co., Japan) in vacuum at 1250 °C for 5 min under 75 MPa and one of them with post-SPS annealing in air at 1100 °C for 12 h. The colour difference between the two ceramics is evident. In particular, it is seen that the as-SPSed ceramic is black, and that it turns white with the post-SPS annealing in air.

Fig. 2A–B shows scanning-electron microscopy (SEM; Quanta 3D FEG, FEI, The Netherlands) images of the fracture surface of the two Ta-doped ZrO_2 ceramics. It is seen that they are dense since essentially there are no pores, and that apparently both ceramics have the same grain size in the submicrometre scale (~100–500 nm). The measurements of grain sizes confirmed that the grain size distributions are similar, and that the mean grain size is ~250 nm in both cases. There are larger grains too, but they appear to contain a grain substructure so that most likely they are actually agglomerates of smaller grains, as has also been observed in Al_2O_3 [34]. It is also seen that their fracture mode is different. Specifically, the as-SPSed ceramic broke in a mixed mode with both transgranular and intergranular fracture, while the post-annealed ceramic broke with intergranular fracture.

Fig. 2C–D shows the same SEM image of the post-annealed Ta-doped ZrO_2 ceramic, taken in both secondary-electron (SE) and backscattered-electron (BSE) modes. The SE image confirms the densification and grain size observations made before on the fracture surface. Most importantly, the absence of contrast in the BSE image indicates that the distribution of O, Zr, and Ta is uniform across the entire microstructure. The elemental maps of O, Zr, and Ta presented in Fig. 3, acquired by X-ray energy-dispersive spectrometry (XEDS) in the SEM, confirm this deduction, by showing that the grains are all equally rich in these three elements. This homogeneity in chemical composition is a result of the wet synthesis of the starting powders by the co-precipitation method.

Fig. 4A shows the X-ray diffraction (XRD; D8 Advance, Bruker AXS, Germany) patterns of the two Ta-doped ZrO_2 ceramics. It is seen that neither of these two XRD patterns corresponds to one of the typical ZrO_2 polymorphs at ambient pressure, that is, to the cubic (Fm3m), tetragonal ($P4_2/nmc$), or monoclinic ($P2_1/c$) polymorphs. They can, however, be ascribed to an orthorhombic ZrO_2 polymorph ($Pca2_1$), an ascription that was further confirmed by the corresponding Pawley

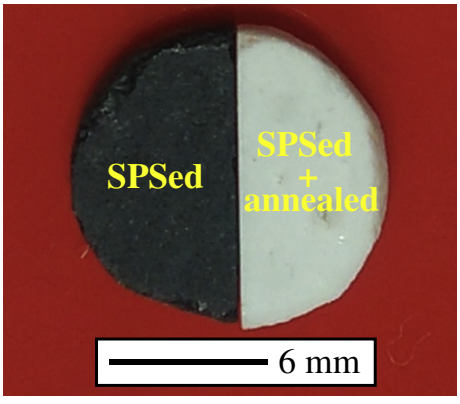

Fig. 1. Optical photograph showing a comparative view of semi-discs of the two Ta-doped ZrO_2 ceramics placed together.

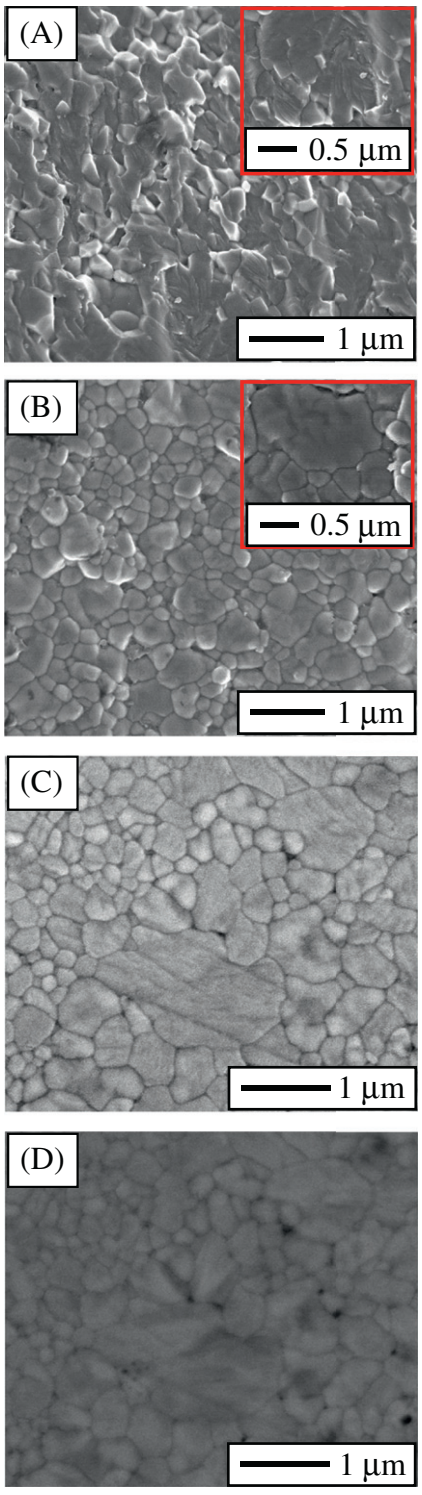

Fig. 2. Representative SEM micrographs of the fracture surfaces of the broken Ta-doped ZrO_2 ceramic (A) in its as-SPSed condition and (B) after the post-SPS annealing in air, and representative SEM micrographs of the thermally-etched, polished surface of the post-annealed ceramic taken with (C) secondary and (D) backscattered electrons. The insets in (A) and (B) are SEM images at higher magnification showing details of the larger grains.