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$ZrTiO_4$ materials obtained by spark plasma reaction-sintering

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ABSTRACT

Zirconium titanate ($ZrTiO_4$), have many attractive properties such as high resistivity, high dielectric constant, high permittivity at microwave frequencies and excellent temperature stability for microwave properties. Zirconium titanate dense materials are proposed for many structural applications, but fully reacted and completely dense pieces are difficult to obtain by conventional routes. In this work, fully dense zirconium titanate materials (~98%) were obtained at lower temperatures (1300–1400 °C) and short processing time by non-conventional technique; spark plasma-reaction sintering (SPRS). Homogeneous and stable starting powders mixture with the adequate composition was prepared from the raw materials: m-ZrO_2 (~0.3 μm) and anatase-TiO_2 (~40 nm). Dense materials were mechanically and microstructural characterised. The fracture strength was measured by biaxial testing, giving values of about 200 MPa.

1. Introduction

Zirconium titanate ($ZrTiO_4$) has been largely used in the field of electroceramics, as constituent of dielectric resonators and components for telecommunications [1–4]. More recently, the synthesis and structural characterisation of zirconium titanate based materials have been studied focusing their high potential for applications requiring resistance to thermal shock, due to its anisotropy in the thermal expansion [5–8]. Synthesis of zirconium titanate powders can be made by different methods like co-precipitation [5,9] (800–1650 °C), sol–gel [10–12] (500–700 °C), mechanochemical processing [13] (room temperature), and solid-state reaction from ZrO_2 and TiO_2 powders [14–16].

Previous works reported the fabrication of single-phase $ZrTiO_4$ bulk materials by conventional sintering [7,16] from submicron-sized m-ZrO_2 and anatase-TiO_2 powders for structural applications. The process involved a two-steps schedule consisting in the slip casting and reaction sintering of ZrO_2 and TiO_2 to form $ZrTiO_4$ and the subsequent milling, isopressing and conventional sintering of those milled $ZrTiO_4$ powders. However, this method has important drawbacks, the most important being, on one hand, that it is a multi-step process which needs long processing times with sintering cycles at 1500 °C and dwell times of up to 16 h and, on the other hand, that the maximum sintered density values attained are up to 94% of theoretical density (T.D.), much lower than desired for structural applications.

Accordingly, not only the green processing must be carefully controlled to improve the homogeneity of the phases but also the choice of the sintering method is crucial to obtain reaction sintered composites with improved properties. In this context fast sintering techniques such as Spark Plasma Sintering have demonstrated their suitability for producing sintered bodies with full density. This technique can work at heating rates of the order of hundreds of degrees per minute, reaching high temperatures in very short time, leading to dense materials after cycles of heating/cooling in the order of a few minutes [17–19]. These features allow achieving microstructures unattainable by other sintering techniques. The manufacture of alumina–aluminium titanate materials by slip casting and electrophoretic deposition (EPD) and further reaction sintering by SPS has been recently described [20,21], thus demonstrating the versatility of this sintering technology.

The main objective of this work was to produce dense single-phase zirconium titanate bulk materials with a direct, simple processing route. For such purpose, submicron-sized m-ZrO_2 and nanosized anatase-TiO_2 powders were selected combining the freeze-drying of well dispersed suspensions to obtain homogeneous mixtures of the powders with a non-conventional sintering process such as spark plasma-reaction sintering (SPRS).

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2. Experimental procedure

Commercial undoped m-ZrO_2 (TZ-0, Tosoh Tokyo, Japan) and anatase-TiO_2 (Aeroxide P25, Degussa, Germany) were used as starting powders to obtain $ZrTiO_4$ materials. Starting zirconia and anatase powders have average particle diameters of 300 nm and 40 nm, and specific surface areas of 14 $m^2 g^{-1}$ and 52 $m^2 g^{-1}$, respectively. The approach used involves the preparation of a total solids loading suspension of 30 vol.%, with 15 vol.% of m-ZrO_2 and 15 vol.% of a-TiO_2, using a poly(acrylic acid) based polyelectrolyte (Duramax D3005 Rohm and Haas, USA) as a dispersant to a total concentration of 5.2 wt.% on a dry solids basis. This high content of deflocculant is due to the nanometric size of titania that can be effectively dispersed with a concentration of 4 wt.% as demonstrated in previous work [22].

For the preparation of the materials, m-ZrO_2 powders were firstly added to the proper amount of distilled water containing the dispersant with the help of a high shear mixer (L2R, Silverson, Chesham, UK). Afterwards a-TiO_2 nanopowders were dispersed with the help of the high shear mixer and an ultrasonic probe (UP 400 S, Hielscher, Stuttgart, Germany). Sonication was performed using several cycles of 1 min, being the maximum sonication time of 8 min and a frequency of 24 kHz, since further sonication cycles led to reagglomeration. The final suspension was frozen in a liquid nitrogen bath and then dried in a freeze drier (Cryodos-50, Telstar, Spain) for 24 h.

Powders obtained were sieved using a 37 μm mesh nylon sieve and introduced into a 20-mm-diameter graphite die and sintered using a spark plasma sintering method (SPS), HP D25/1 apparatus (FCT Systeme GmbH, Rauenstein, Germany) at temperatures from 1300 to 1400 °C and 80 MPa of applied pressure to obtain fully sintered bulk materials. Tests were carried out under vacuum at a heating rate of 100 °C min^{-1} with a 1 min of dwelling time at the maximum temperature.

Sintered density was determined by the Archimedes' method (ISO-3369) using deionized water.

The crystalline phases present were determined by X-ray diffraction. The obtained XRD patterns were analysed using the diffraction files of $ZrTiO_4$ (PDF: 00-034-0415, density = 5.08 g cm^{-3}) and m-ZrO_2 (PDF: 00-037-1484, density = 5.82 g cm^{-3}). Patterns for profile fitting using the Rietveld method [23] were obtained from a diffractometer (Brucker AXS-5005, SCSIE of the University of Valencia) using Cu Kα radiation. Compact pellets were used as samples and mounted in an appropriate sample holder. Patterns were collected with a scanning step of 0.02° between 10° and 110° in 2θ with a collection time of 10 s per step. Profile fittings were performed using the FULLPROF program [24].

The relative ratio between monoclinic zirconia and zirconium titanate was obtained from the profile fittings. Relative density of the sintered materials (% of T.D.) was evaluated considering that the final phases were Zirconium Titanate (ZT) and m-ZrO_2 and taking into account the relative ratio of both phases. Error bars in the calculated densities are within the error of the measurements.

Sintered samples were longitudinally cut in half cylinders with a diamond saw. The samples were previously polished (Struers, model RotoPol-31) with diamond paste to 0.25 μm roughness. Nanomechanical properties such as hardness and Young's modulus of samples were obtained by nanoindentation technique (Model G200, MTS Company, USA). To carry out indentations at very low depths, a brand new Berkovich diamond tip was used with radius less than 20 nm as certified by the manufacturing company. In order to ensure the quality of the tip throughout the work, pre- and post- calibration procedures were performed for this indenter ensuring the correct calibration of its function area and correct machine compliance. The nanomechanical properties of the $ZrTiO_4$ ceramics were evaluated from the load–displacement nanoindentation data using the widely accepted Oliver and Pharr model [25].

The flexural strength was measured by biaxial testing using the equations of Kirstein and Woolley [26], Vitman and Pukh [27], and the standard specification ASTM F394-78. All tests were obtained at room temperature using a universal testing machine (Instron 856, MA, USA) with a cross-head displacement speed of 0.002 mm s^{-1}. The fracture surface sections of the sintered samples have been observed using a field emission gun scanning electron microscope (FE-SEM, HITACHI S-4800, SCSIE of the University of Valencia).

3. Results and discussion

XRD patterns of the bulk ceramic $ZrTiO_4$ materials (ZT) sintered by spark plasma reaction-sintering (SPRS) at 1300, 1350 and 1400 °C are shown in Fig. 1. They show that it is possible to obtain $ZrTiO_4$ materials at lower temperature than that used during normal solid-state reaction sintering [7,28]. Reflections at $2\theta \sim 28°$ and 31° show the presence of residual m-ZrO_2, whereas it is not possible to observe characteristic peaks of TiO_2.

It must be stressed that ZrO_2/TiO_2 ratio used to prepare green compacts was calculated to obtain single-phase zirconium titanate materials [7,16].

If ZT phase obtained would be stoichiometric (i.e., $ZrTiO_4$), the presence of residual m-ZrO_2 should be accompanied by residual TiO_2. However, we have not observed TiO_2 XRD peaks in the diffraction pattern, which could be attributed to its low relative intensity.

Nevertheless, investigations in the phase diagram of ZrO_2–TiO_2 show the existence of a disordered $Zr_{1-x}Ti_{1+x}O_4$ at temperatures above i.e. 1150 °C. The presence of m-ZrO_2 is compatible, then, with a ZT phase with a Ti/Zr ratio $(1+x)/(1-x)$ greater than 1. The situation can be, indeed, more complicated due to the significant solubility of Ti in ZrO_2 at such temperatures.

In order to determine the m-ZrO_2 content and the Ti and Zr stoichiometry in the ZT phase, we have performed profile fittings of XRD patterns of the samples. Summarised in Table 1 are the main data obtained for the samples prepared at 1300, 1350 and 1400 °C. The fits were performed considering a mixture of $Zr_{1-x}Ti_{1+x}O_4$ and m-ZrO_2 phases. Although we have indicated above the significant solubility of Ti in ZrO_2 at high temperatures, the low intensity of the zirconia reflections precludes the evaluation of the Ti present in the m-ZrO_2 by such analysis. A pseudo-Voigt peak-shape function was used. In the final runs, the usual profile parameters (scale factors, background coefficients, zero-points, half-width, pseudo-Voigt and asymmetry parameters for the peak-shape) were refined. Cell parameteres, atomic positions and x were refined for $Zr_{1-x}Ti_{1+x}O_4$. However, for m-ZrO_2, due to the low intensity of its reflections, only cell parameters were refined. Isotropic thermal parameters were set at 0.5 and 0.9 $Å^2$ for metal and oxygen atoms, respectively, and an overall thermal parameter was also refined for each phase.

Cell parameters for ZT showed in Table 1 are close with data reported previously for $ZrTiO_4$ air quenched from the sintering temperature [7], which indicate that the cooling rate of SPS is very high.

We have made the refinements considering a disordered ZT phase. Such assumption is reasonable taking into account that we have not observed the characteristic superstructure reflections of the ordered phase. In addition, b cell parameter, a well-known indicator of the state of ordering in ZT phase [15], have values typical of disordered phases in all the samples.

The calculated m-ZrO_2 content is around 9% for samples prepared at 1300 and 1350 °C, and decreases to 3.9% for the samples