J.G.Heinrich and C. Aneziris, Proc. 10th ECerS Conf., Göller Verlag, Baden-Baden, 2007, 866-870, ISBN: 3-87264-022-4

Zirconium Titanate Ceramics for Humidity Sensors Synthesized by Sol-Gel Process

J. Macan[1,*], A. Gajović[2], D. Dekanić[1], H. Ivanković[1]

[1] University of Zagreb, Faculty of Chemical Engineering and Technology, Marulićev trg 19, P.O. Box 177, HR-10000 Zagreb, Croatia
[2] Ruđer Bošković Institute, Materials Physics Department, Molecular Physics Laboratory, Bijenička 54, P.O. Box 180, HR-10002 Zagreb, Croatia

Abstract

Zirconium titanate, $ZrTiO_4$ was synthesized by sol-gel method from zirconium butoxide and titanium isopropoxide. Amorphous $ZrTiO_4$ powder was ground to under 0.8 mm, calcined at 500 °C, and milled to homogenise size distribution of the powder. Milled powder was pressed into tablets and sintered at 900-1400 °C for 8 hours. Differential scanning calorimetry and dilatometric studies indicated crystallization of $ZrTiO_4$ at 600-700 °C. Raman spectroscopy and X-ray diffraction analysis confirmed crystallization of pure zirconium titanate already at 900 °C, and crystallite size was determined by Scherrer equation. Scanning electron microscopy showed that $ZrTiO_4$ grains begin to sinter at higher temperatures, starting from 1200 °C, while preserving high porosity up to 1300 °C.

Keywords: porosity, sensors, sintering, sol-gel process, zirconium titanate

Introduction

Zirconium titanate, $ZrTiO_4$, is a ceramic material with very good thermal and electrical properties and high resistance to heat and corrosive environment. This lead to its widespread use in electronic components for telecommunication purposes (condensers, resonators, etc) [1] and catalysts [2,3]. Lately applicability of zirconium titanate for humidity sensors is also being investigated [4]. For all these applications, high purity and homogeneity of ceramic material is essential. This is difficult to achieve by classical procedure of firing a stoichiometric mixture of zirconia, ZrO_2, and titania, TiO_2, powders at temperatures up to 1600 °C for several days [1,5]. High-energy milling of ZrO_2 and TiO_2 to reduce crystallite size and give almost amorphous powders can lower the transition temperature as low as 1100 °C [6-8]. But this approach is also energy costly, and attrition of milling balls can increase content of impurities [6,8]. Therefore sol-gel process, which consists of hydrolysis and condensation of metal chlorides [3,9] or alkoxides [2,10,11] to form oxide ceramics, is increasingly used to prepare homogeneous and amorphous $ZrTiO_4$ powder, which crystallizes at temperatures several hundred degrees lower than in previous methods. Ceramics synthesized by sol-gel process are also very pure and their microstructure is comparatively easy to tailor.

Previous research of $ZrTiO_4$ ceramic bodies, sintered from powder prepared by high-energy ball milling of ZrO_2 and TiO_2, has shown that electrical conductivity in humid air is highly dependant on porosity [12]. In this work $ZrTiO_4$ amorphous powder was prepared by sol-gel process from zirconium and titanium alkoxides, pressed into tablets and sintered at different temperatures. The influence of temperature on sintering behaviour and microstructure of prepared $ZrTiO_4$ ceramics was studied.

Experimental

Zirconium titanate, $ZrTiO_4$, was synthesized by sol-gel method from zirconium butoxide ($Zr(C_4H_9O)_4$, 80 %) and titanium isopropoxide ($Ti(C_3H_7O)_4$, 97 %), stabilised with acetilacetone and hydrolysed with stoichiometric amount of water, with nitric acid as catalyst. Transparent sol was left to gel at room temperature. The gel was dried at 110 °C, ground and sieved to remove particles larger than 0.8 mm, calcined at 500 °C to remove residual organic content, and milled. Milling was performed for 2 hours in air using a Fritsch planetary ball mill Pulverisette 6 with vial and balls of 94 % zirconia, with rotation speed of 500 rpm and powder-to-ball weight ratio of 1:10. Specific surface area of milled and non-milled powder, previously degassed overnight at 250 °C, was determined by inverse BET method from nitrogen adsorption-desorption isotherms at liquid N_2 temperature on a Micromeritics ASAP 2000, from measurements at 5 relative pressures of nitrogen in 0.05-0.21 range. Amorphous powders were observed by transmission electron microscopy (TEM) on microscope JEOL JEM-200CX with tungsten cathode operating at accelerating voltage of 200 kV. Thermal behaviour of the milled powder was studied by simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC-TGA) on a Netzsch thermoanalyzer STA 409. Sample was heated from room temperature to 1350 °C at a heating rate of 10 °C/min in a synthetic air flow of 30 cm^3/min.

Milled powder was uniaxially pressed (180 MPa) into tablets of 13 mm diameter and sintered for 8 hours in a muffle furnace with Pt-PtRh thermocouple at 900, 1100, 1200, 1300 and 1400 °C. Furnace was heated to sintering temperature at 23 °C/min.

Raman spectroscopy measurements were performed using a computerized DILOR Z24 triple monochromator with Coherent Innova 400 argon ion

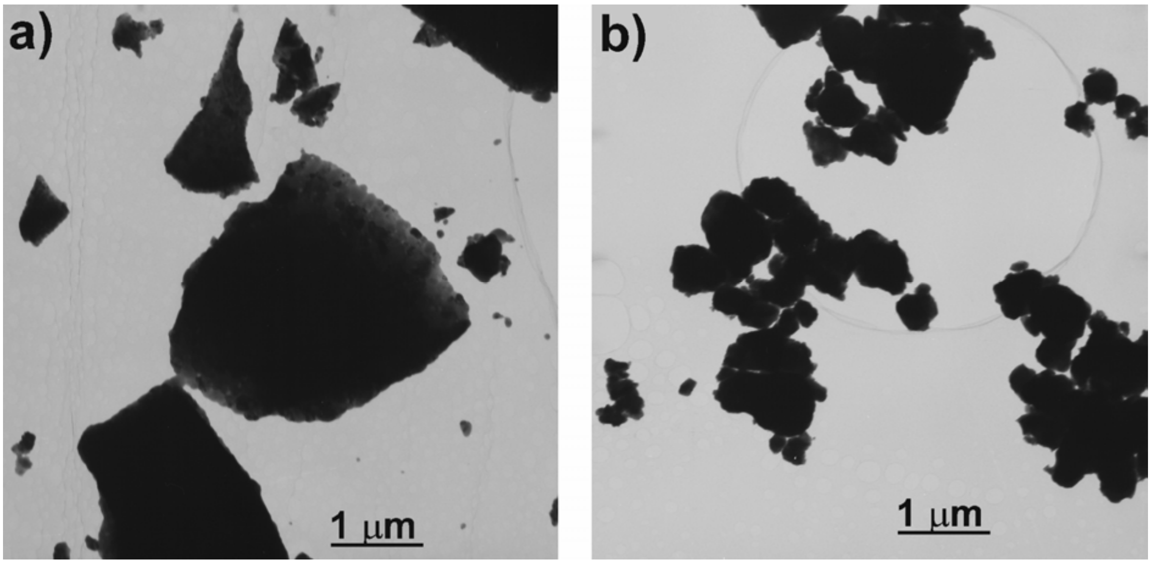

Figure 1 – Transmission electron micrographs of a) unmilled and b) milled amorphous $ZrTiO_4$ powder

laser operating at 514.5 nm for excitation, applied laser power was 150 mW. To reduce the heating of the sample during measurement, the incident laser beam was focused in the line shape. X-ray powder diffraction (XRD) analysis was performed on Phillips PW 1820 instrument making use of CuKα radiation with a scanning rate of 0.12°/min. Thermodilatometric study was carried out on uniaxially pressed (250 MPa) compacts (10 × 3 × 3 mm) using horizontal-loading differential dilatometer Netzsch DIL 402ED operating at 5 °C/min heating rate. Scanning electron microscopy (SEM) of sintered gold-coated samples was performed on JEOL T300 microscope operating at 25 kV.

Results and discussion

Milling of amorphous powder homogenizes its size distribution, as can be seen from TEM micrographs (Figure 1), but also causes agglomeration and decrease of specific surface to 12.2 m^2/g, compared with 83.2 m^2/g of unmilled powder. Average particle size of milled powder as determined by TEM is in the 0.25-1 μm range. The milled powder was chosen for further investigation to ensure homogeneity of particle size distribution.

Results of DSC-TGA analysis are given in Figure 2. The first mass loss evident on the TGA curve and accompanied by a DSC endothermic maximum at 83 °C is due to evaporation of adsorbed water. The mass loss decreases approximately constantly with further temperature increase, which is ascribed to slow degradation of residual organic content. Large DSC exothermic maximum at 703 °C is due to crystallization of amorphous $ZrTiO_4$, as confirmed by our preliminary research. Raman spectroscopy (Figure 3) and XRD analysis (Figure 4) confirm that samples sintered at 900 °C and higher temperatures are crystalline $ZrTiO_4$.

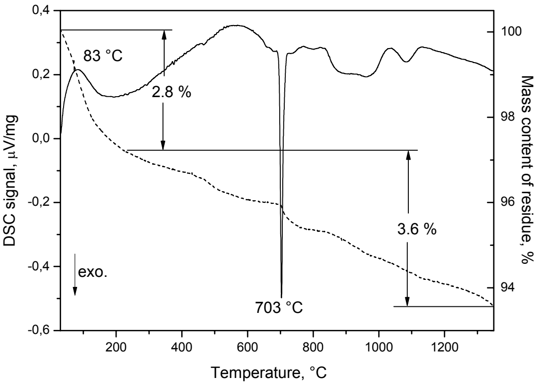

Figure 2 – Combined differential scanning calorimetry and thermogravimetric analysis of $ZrTiO_4$ amorphous powder calcined at 500 °C, measured in air at 10 °C/min

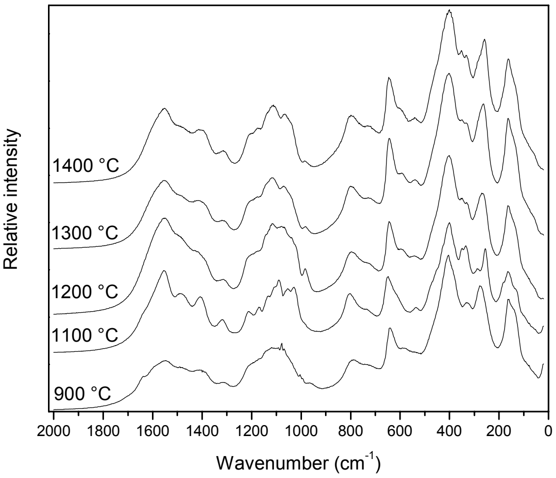

Figure 3 – Raman spectra of $ZrTiO_4$ tablets sintered for 8 hours at temperatures denoted above spectra.

$ZrTiO_4$ with orthorhombic symmetry (space group *Pbcn*) and two formula units in a unit cell has 33 optically active modes of vibration, 18 of which are Raman active. Only $ZrTiO_4$ bands were observed in 20-900 cm^{-1} region of the Raman spectra of sintered ceramics (Figure 3). The bands for all the samples are broad, which can be attributed to random distribution of Zr^{4+} and Ti^{4+} ions in equivalent sites of crystal lattice, oxide defects and nonstoichiometric variations of Zr/Ti ratio in polycrystalline ceramics [13,14]. Number of resolved Raman bands varies with sintering time, indicating differences in structural order [13]. In the Raman spectrum of the sample sintered at 1100 °C, 12 out of 18 expected $ZrTiO_4$ bands were resolved: 132, 160, 256, 286, 332, 404, 468 (shoulder), 536, 588 (shoulder), 640, 730 and 804 cm^{-1}. It should be noted that the bands at 256 and 286 cm^{-1} were resolved only in this sample, but the band at 588 appeared only as a shoulder. A band at 350 cm^{-1} that does not belong to $ZrTiO_4$ was observed in the Raman spectra of all sintered ceramics. Additional intensive part of spectra was detected at wavenumbers higher than 1000 cm^{-1}. These additional bands do not appear in unpressed powdered samples calcined in the same conditions (not shown), so it is supposed they are caused by residual organic groups inside the pores. Presence of residual organic components at higher temperatures is also obvious from constant mass loss in TGA curve (Figure 2). Further investigation of this effect is planned.

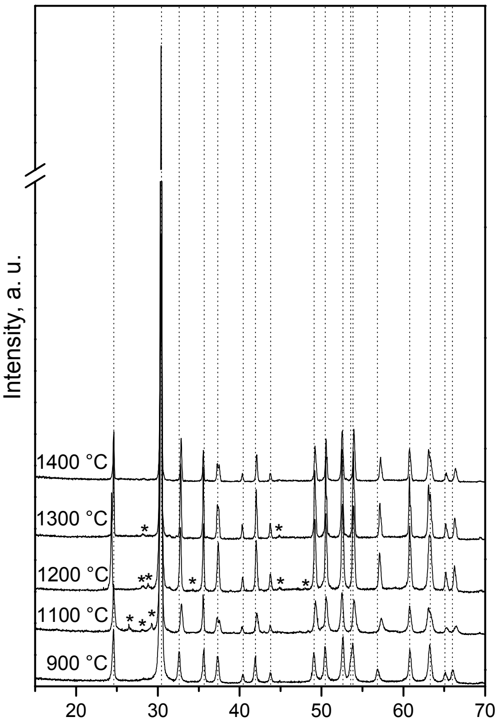

Figure 4 – X-ray diffractograms of $ZrTiO_4$ tablets sintered for 8 hours at denoted temperatures; JCPDS data for zirconium titanate (34-415) shown as dotted lines, and as yet unidentified crystalline phases marked with *

XRD measurements confirm that all sintered ceramics crystallize in orthorhombic symmetry, as indicated in Figure 4 by dotted JCPDS data lines for zirconium titanate (34-415). Samples sintered at 1100-1300 °C contain minute amounts of other, as yet unidentified crystalline phases, marked with * on the figure. Detailed investigation of crystallization of sol-gel $ZrTiO_4$ tablets and powder is in progress. Increase in sintering temperature promotes crystallite growth, which is apparent from decreased width and increased intensity of XRD maxima. Average crystallite size was determined from broadening of the XRD maxima by Scherrer equation (Table 1), using $ZrTiO_4$ crystallized at 1500 °C for 5 hours as a standard to correct for the instrumental broadening. The strain contribution to the broadening could be neglected in the calculation at low Bragg angles [15]. The apparent crystallite size decreases at highest sintering temperature of 1400 °C, which could be a consequence of additional strain in the material due to marked volume shrinking at this temperature.

Table 1 – Crystallite size as determined by Scherrer equation

Temperature, °C	Crystallite size, nm
900	38 ± 2
1100	45 ± 14
1200	66 ± 22
1300	220 ± 40
1400	100 ± 20

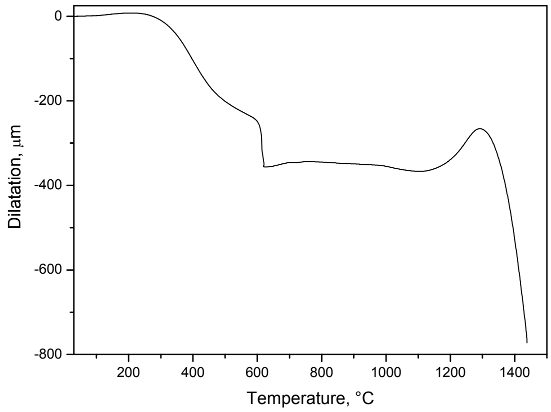

Figure 5 – Dilatometric curve for amorphous pressed $ZrTiO_4$ sample heated at 5 °C/min

Dilatometric curve (Figure 5) shows that, after initial shrinking due to removal of organic components, sample suddenly shrinks at 614 °C. This corresponds to crystallization of $ZrTiO_4$, shifted to lower temperature than in DSC curve due to slower heating rate. Additional shrinking after 1300 °C is caused by sintering of porous $ZrTiO_4$ into a dense ceramic body. This is confirmed by SEM micrographs of surfaces and inner side of tablets (Figure 6), which also show grain growth with increased temperature of sintering. It can be seen that grains start to sinter together at 1200 °C and still retain very high porosity up to at least 1300 °C. Increased temperature of sintering also increases mechanical strength of tablets: while tablets sintered at 900 °C crumble easily, those fired at 1200 and 1300 °C

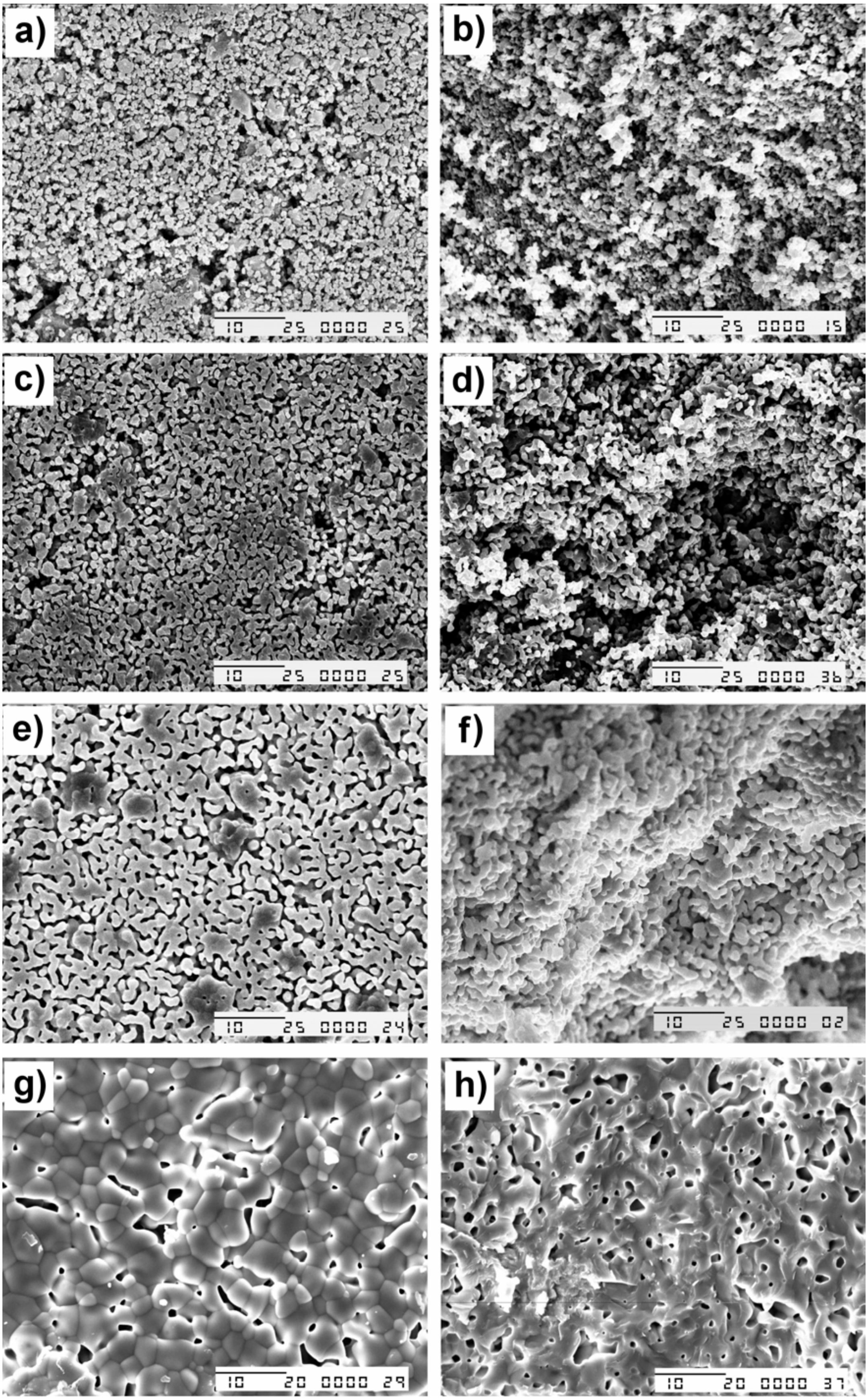

Figure 6 – SEM micrographs of surfaces and inner side of tablets sintered at 1100 °C (a, b), 1200 °C (c, d), 1300 °C (e, f) and 1400 °C (g, h); scale bar is 10 μm

are much more resilient in spite of their high porosity. Therefore, sol-gel process shows potential for preparation of porous $ZrTiO_4$ ceramic bodies for humidity sensors.

Conclusions

Porous zirconium titanate ceramic was prepared from zirconium and titanium alkoxides by sol-gel process. The ceramic bodies were prepared by sintering of the amorphous powder precursor, which was previously homogenized by milling to particle sizes between 0.25 and 1 μm. Amorphous powders crystallize at temperatures of 600-700 °C, depending on heating rate. Porosity of the ceramic bodies was tailored by changing the sintering temperature. Samples do not start to lose their porosity until temperatures higher than 1300 °C. It is therefore possible to prepare fully crystallized porous $ZrTiO_4$ ceramic in this manner.

Acknowledgments

Authors would like to thank the Ministry of Science, Education and Sport of the Republic of Croatia for the financial support of this study, which is a part of research projects “Bioceramic, Polymer and Composite Nanostructured Materials”, 125-1252970-3005 and “Physics and applications of nanostructures and bulk matter”, 098-0982904-2898. The authors would also like to thank Mr. J. Schmauch, University of Saarland, Germany, for performing thermodilatometric analysis.

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