

## **Zirconium titanate: synthesis and processing of fine powders prepared by chemical route**

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Abstract. A process for synthesis of fine zirconium titanate powders by chemical route is described. Zirconium/titanium molar ratio was varied from 0.67 to 1.5 and the powders produced were analyzed. The precipitation process comprises the mixture of zirconium and titanium metal salt solutions to ammonium hydroxide solution, followed by washing of the precipitate, calcination and grinding to result in zirconium titanate. The ceramic powder is then uniaxially pressed as cylindrical samples and sintered at 1400°C for 5 hours. The microstructure of fractured and thermally etched ceramic was observed by scanning electron microscopy, and crystal phase identifications were done by X-ray diffraction. At least two different zirconium titanate phases,  $ZrTiO_4$  and  $Zr_5Ti_7O_{24}$ , were identified. Ceramic hardness was measured by Vickers indentation.

### **Introduction**

Titania ceramic powders are widely used as pigment and catalyst. These features are presented mainly by the anatase polymorph, a metastable phase of  $TiO_2$ . The transformation to the thermodynamically stable rutile phase, from temperatures low as 500°C, is known to degrade the surface properties of titania ceramics [1].

Zirconia ceramics also has good properties as catalyst and pigments, and excellent mechanical properties that make it suitable for catalyst support. Three thermodynamically stable polymorphs of zirconia exists in different temperatures ranges. The monoclinic phase, stable from room temperature to about 1100°C, transform to tetragonal phase at 2400°C, and above this temperature transform to cubic symmetry [2]. The monoclinic and tetragonal phases have different catalytic activity. Dopants of di or trivalent cations can stabilize the metastable tetragonal or cubic phase in room temperature, but this additives can affect the electric properties of the ceramic. Besides that, titania, when used as zirconia dopant has low solid solubility in zirconia and stabilize zirconia tetragonal phase. Thus, taking advantage of good properties of both ceramics and in order to avoid its drawbacks, many researches of the zirconia-titania ceramic system have been published[3],[4]. The ceramic system of the mixture of zirconia and titania form preferably zirconium titanate solid solution.

Zirconium titanate has the orthorhombic structure of  $\alpha$ - $PbO_2$  and belongs to the space group  $Pbcn$  [5]. The high temperature  $ZrTiO_4$  phase has a random cation distribution on the available sites, and on cooling there is a sluggish order-disorder transition to the low temperature phase at 1200-110°C [6],[7]. Zirconium titanate melts incongruently at 1760 °C and is known to have a high temperature structure  $ZrTiO_4$  with disordered cations distribution in the octahedral sites. On

cooling, a transition occurs approximately at 1150°C, with formation of titanium rich compound  $Zr_5Ti_7O_{24}$ , that has also the  $\alpha$ - $PbO_2$  structure, with progressive ordering of  $Zr^{4+}$  and  $Ti^{4+}$  and a zirconium rich compound is exsolved to attain the chemical equilibrium. In samples cooled very slowly, the formation of the titanium rich compound is increased and in samples with titania excess, some grains of this compound can crystallize out of ceramic surface [7].

$ZrTiO_4$  has excellent dielectric properties and thermal stability to relatively high temperatures as 1400°C, with good properties for use as catalyst. It also finds extensive application in microwave telecommunication devices as capacitors and dielectric resonator and also find use as high temperature pigments and composites[8],[9]. To ensure these properties and the chemical stoichiometry, the starting ceramic powders has to be fine grained and chemically homogeneous. Chemical routes are excellent alternatives and the resulting powders have also good sintering properties and lower costs due to simpler post reaction treatments. In the present work, a coprecipitation technique of aqueous solution of titanium and zirconium chlorides in ammonium hydroxide was employed. The zirconium/titanium rate was varied and its influence on crystal structure and microstructure of the ceramics was studied. To evaluate ceramic hardness, Vickers indentation tests were carried out.

## **Experimental procedure**

### **Sample preparation**

Zirconium oxychloride solution was prepared from zirconium hydroxide produced in the Zirconium Plant of IPEN and titanium chloride solution was prepared in our laboratories from commercial titania powder [10]. The zirconium/titanium ratio was fixed at 1.5; 1.22; 1.0; 0.82; and 0.67 and these samples were named ZT1; ZT2; ZT3; ZT4 and ZT5, respectively. These mixtures were added to ammonium hydroxide solution, filtered, washed and distilled with n-butyl alcohol. The powders dried for about 10 hours at 80°C, deagglomerated in agate mortar, calcined at 800°C for 1 hour and milled with zirconia balls for 15 hours. The powders were uniaxially pressed in cylindrical dies (100 MPa) and sintered at 1400°C for 4 hours. Fractured and thermally etched ceramic surface was observed by scanning electron microscopy (SEM-Phillips XL 30) and X-ray diffraction patterns of polished specimens were registered using  $CuK\alpha$  radiation (Rigaku DMAX 2000). Ceramic hardness was measured in polished samples with a Vickers indentator (Buehler VMT-7).

### **Results and discussion**

SEM micrographs of fractured surface of ceramic samples are shown Fig 1. It can be seen that variation of the zirconia/titania ratio changes the microstructure and the fracture behavior. Sample ZT1 (a) shows large pores and rounded grains, indicating the predominance of intergranular fracture. Larger fractured surface and smaller pores can be seen in the sample ZT2 (b). This behavior is more pronounced in sample ZT3 (c). Samples ZT4 (d) and ZT5 (e) show very little pore quantity, smaller grain size and prevailing of intragranular fracture mode.

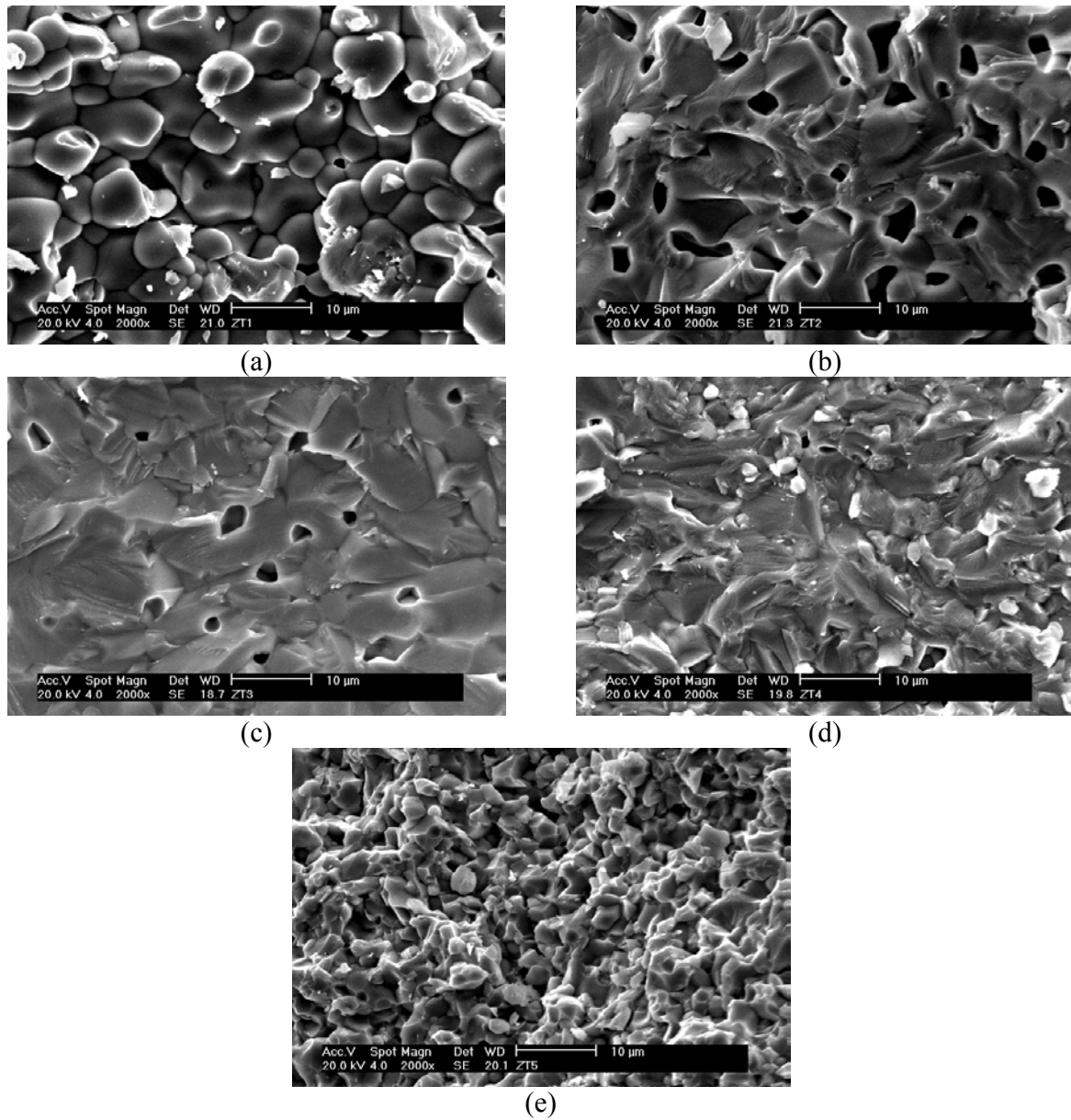


Fig.1. SEM micrographs of fractured ceramic surface of samples ZT1(a); ZT2(b); ZT3(c); ZT4(d) and ZT5(b).

This result shows that in these samples, the higher is the titania concentration, worse is the ceramic sinterability. On the other hand, when higher is the zirconia concentration smaller are the grains size and more uniform is the fracture surface.

Polished ceramic was thermally etched at 1350°C for 30 minutes and the SEM micrographs of this samples are shown in Fig. 2. The observation of these microstructures confirms the progressive reduction of porosity and grain size. In addition, it can be seen that the exsolvated grains crystallizes over the thermally etched surface. Probably, zirconium rich compound is originated from the reordering of zirconium titanate.

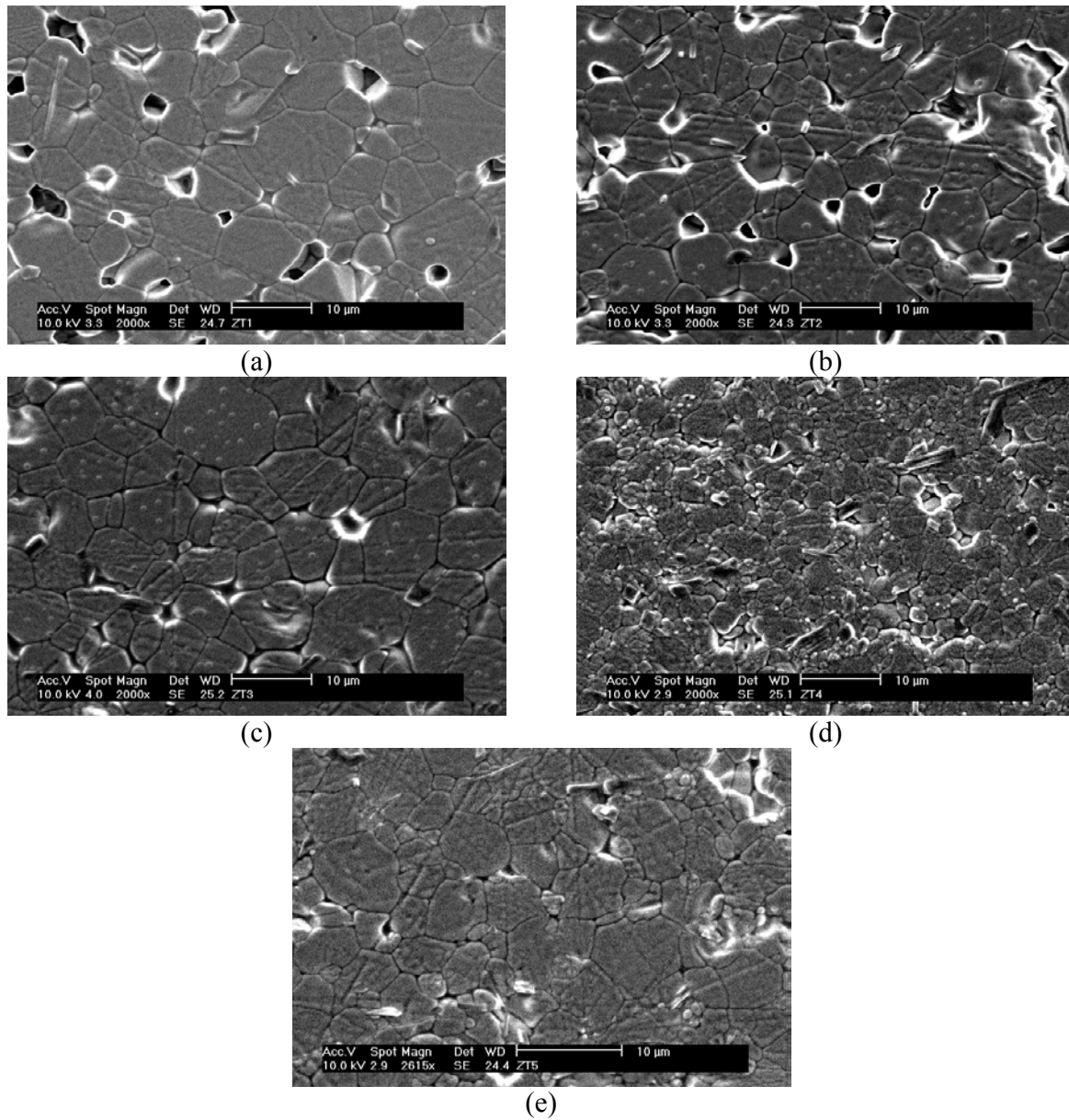


Fig.2. SEM micrographs of polished and thermally etched ceramic surface of samples ZT1(a); ZT2(b); ZT3(c); ZT4(d) and ZT5(e).

X-ray diffraction pattern of the samples are shown in Fig. 03 and the observed reflections are compared with ICDD files for the compounds  $ZrTiO_4$  (34-415);  $Zr_5Ti_7O_{24}$  (34-209) and Baddeleyite, the monoclinic  $ZrO_2$  phase (37-1484). It can be seen that in all samples the predominant reflections are those of  $ZrTiO_4$  phase. In ZT1 sample, some  $Zr_5Ti_7O_{24}$  reflections are also observed. In samples ZT2 and ZT3 only the  $ZrTiO_4$  reflections are present, while in specimens with higher zirconia concentration,  $ZrTiO_4$  and Baddeleyite reflections were observed. These reflections became stronger in sample ZT5.

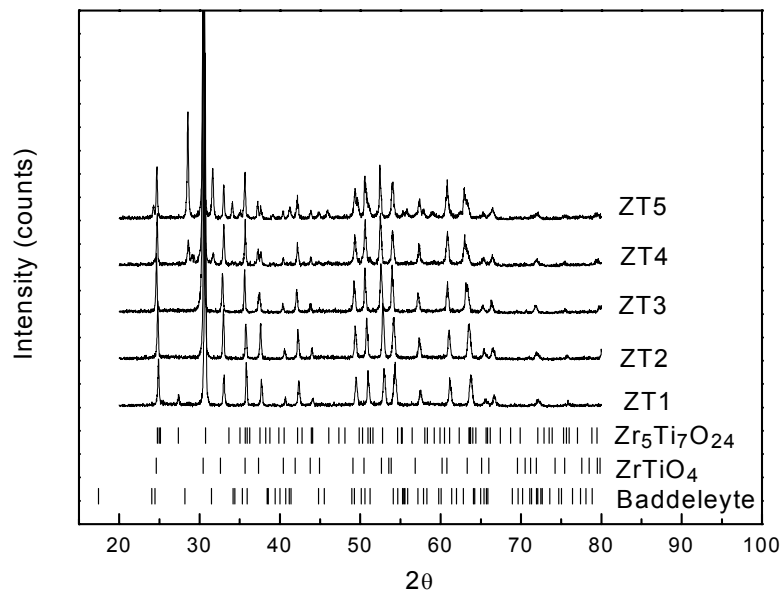


Fig.3. X-ray diffraction pattern of polished ceramics, compared with ICDD data for  $ZrTiO_4$ ,  $Zr_5Ti_7O_{24}$  and Baddeleyite.

Vickers hardness measurements were carried out on polished samples and the results were plotted against the zirconia/titania ratio in the graph shown in Fig. 4. It can be seen that hardness is higher for higher zirconia concentration. These results indicate that the fracture mode, porosity and grain size, as shown in Fig.1, are directly related to the hardness of the ceramic samples. Best results are associated with less porosity, smaller grains and intragranular fracture.

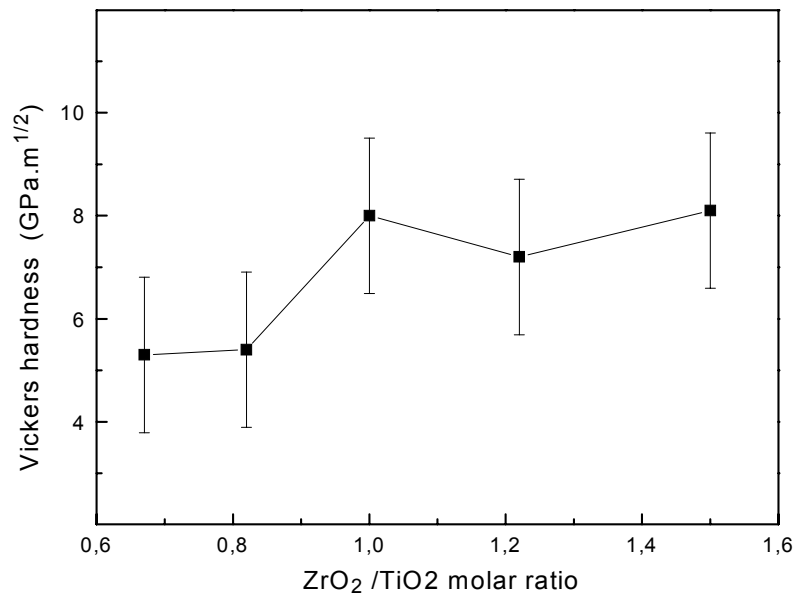


Fig.4. Vickers hardness of polished ceramics  $ZrO_2$  as a function of molar concentration.

## Conclusion

Zirconium titanate ceramics can be produced by aqueous coprecipitation process with good reproducibility and low cost post-treatment. Variation of the zirconium/titanium ratio resulted in ceramics with different crystal structures and microstructure; which affect its mechanical property. Although ceramics with good physical characteristics could be prepared, it became clear, from the results, that the phase relationship in this system is more complex, as can be seen from the formation of exsolved grains. Transition to the low temperature  $Zr_5Ti_7O_{24}$  phase seems to be very slow and need to be studied using thermal treatments with very long cooling time. Otherwise, the effect of the presence this the phase on the electrical properties has also to be cleared.

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