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# SYNTHESIS OF 3MOL% YSZ BY CO-PRECIPITATION METHOD & INFLUENCE OF PROPANOL WASH

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**Abstract:**

Influence of propanol treatment of co-precipitated yttrium–zirconium hydroxide on deagglomeration of calcined nano 3YSZ powder was studied. Results indicated that the amount of propanol used in washing the zirconium hydroxide precipitate had a significant impact on the calcined powder characteristics.

Different ratios of propanol to the water contained within the precipitate were used during washing and the calcined nano 3YSZ powders were characterized in XRD & CHN analysis. Nanocrystalline 3YSZ (3 mol% yttria stabilized zirconia) powders were synthesized through co-precipitation followed by washing with propanol and calcination at different temperatures in the range of 100˚–500 °C.

The powders calcined at different temperatures showed apparent differences in the state of agglomeration. Besides the use of conventional techniques, such as CHN analysis for percentage of elements Carbon,Hydrogen & Nitrogen,X-ray powder diffraction(XRD) for phase analysis,TEM(Transmission Electron Microscope) for agglomeration state, ,FTIR(Fourier Transform Infrared Spectroscopy) is an analytical technique used to identify organic (and in some cases inorganic) materials.Results were studied.

**Keywords:**

3YSZ(3mol% yttria stabilized zirconia),Co-precipitation method,Agglomeration,Temperature,Powders

## 1.Introduction:

Zirconia ceramics have received a lot of attention from researchers due to their unique properties associated with different crystalline forms. Zirconia stabilized in tetragonal form is suited for structural applications owing to its high fracture toughness, strength whereas
zirconia stabilized in cubic form has been used in fuel cells, sensors etc. because of its high oxygen ion conductivity and phase stability[1-38].Besides the inherently high fracture toughness of the tetragonal phase, higher strengths in tetragonal zirconia have been achieved by producing submicrometer size grains in highly dense sintered ceramics.To achieve this, the starting powder particles have to be in the nanoscale (<100 nm) so that on consolidation and sintering they attain high densification with submicrometer grain size. Over the years many approaches have been developed for synthesis of partially or fully stabilized nanocrystalline zirconia ceramics but controlling the state agglomeration in nanocrystalline powders has remained a challenge. The extent of agglomeration in nanoceramic materials has been seen to be a function of the synthesis route including the temperature of calcinations of amorphous intermediates which result in crystallization. Hydrothermal synthesis typically does not involve high temperature calcinations and thus results in lower extent of agglomeration of particles[1-11]. Zirconia is a white powdered material commonly used to produce dental frameworks for dental substructures such as crowns, bridges, etc. Unlike standard ceramics that tend to be brittle and hard, Zirconia has excellent wear resistance and strength, and comes with a flexibility which is far better than those of other technical ceramics.Pure zirconium dioxide undergoes a phase transformation from monoclinic (stable at room temperature) to tetragonal (at about 1173 °C) and then to cubic (at about 2370 °C), according to the scheme(Figure 1).

Monoclinic (1173 °C)→ Tetragonal (2370 °C) →Cubic (2680 °C)→ Melt

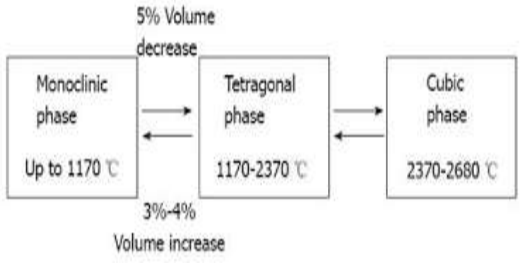


Figure 1:Phase transformation of Zirconia

Nanocrystalline zirconia has been synthesized by various chemical routes but among them coprecipitation method has been popular as it can be scaled up,using low-cost accessories. In this method, the step of driving away water from coprecipitated mass, forces theparticles to agglomerate. The follow-up step of hightemperature treatment1 (crystallization) leads to further
enhancement and strengthening of agglomerates.[12-35].Heuer et al.[36] reported that during drying of the coprecipitated mass, high surface tension of water (73 mN/m) is responsible for bringing the zirconium hydroxide nanoparticles closer resulting in hard agglomerates. If ethanol is used for surface treatment of zirconium hydroxide precipitate, the extent of agglomeration
reduces considerably because of its low surface tension (24 mN/m). On drying, particles are not forced together and the hydroxyl bridging as encountered in case of water-washed powder is missing and hence

result in lower degree of agglomeration.[39-53].Wang et al.[48] reported the synthesis of zirconia with 80% of ethanol added after dissolution of $ZrOCl_2.8H_2O$ in minimum water to get rid of agglomeration problem to a considerable extent. In his work12 10 mol% $MgO–ZrO_2$ was synthesized by coprecipitation by using mixed solvent (water and ethanol)
and pure ethanol. In both cases the final precipitate was washed with absolute ethanol.Initial studies by the present authors while confirming the prior observations that ethanol washing
contributes to deagglomeration suggested that amount of ethanol used in washing of coprecipitated mass may have a role in determining calcined (crystalline) powder characteristics, however, the aspect of washing with Propanol as not been reported in the literature. H.G.SCOTT et.al[33] worked on Phase relationships in the zirconia—yttria system wherein the Metastable and Equilibrium phase relationships in the system $ZrO_2$:$YO_{1.5}$ have been studied by X-ray diffraction.The conditions for the retention of a zirconia-rich tetragonal phase at ambient temperature are established.The existence of a miscibility gap,closed below the solidus temperature,in the yttria-rich solid solution region is proposed.some evidence for partially ordered phases is presented. MARY SUE KALISZEWSKI & ARTHUR H. HEUER et.al[38] worked on the Alcohol interaction with zirconia powders wherein the mechanism by which alcohol washing of ceramic powders produces “soft” agglomerates has been investigated by studying the interaction of ethanol with hydrous $ZrO_2$ powders using Fourier transform infrared (FTIR) spectroscopy. Unambiguous evidence of ethoxide formation has been found, which apparently prevents bond formation between adjacent particles and thus the formation of “hard” agglomerates

**2.Experimental Method**:Co-Precipitation Method is used for synthesis,it is a phenomenon where a solute that would normally remain dissolved in a solution precipitates out on a carrier that forces it to bind together,rather than remaining dispersed.The simultaneous precipitation of more than one componenet(Figure 2).


Figure 2:Flow chart of Co-precipitation method

**Materials used:**Zirconium Oxychloride(Mincometsal ,Bangalore),Yttrium Nitrate(Mincometsal,Bangalore),Ammonia, Deionized water & 1-Propanol.

**Synthesis Process:**The synthesis of 3mol% yttria-stabilized zirconia carried out after trial with 0.1MPrecursor solution & Precipitate(a),0.125M Precursor solution & Precipitate(b),0.2M Precursor solution & Precipitate(c),0.5M Precursor solution & Precipitate(d) & 1M Precursor solution & Precipitate(e) wherein 0.5M was confirmed and the precipitate obtained(Figure 3).

Figure 3:Different molar concentration

Synthesis of 3 mol% yttria–stabilized zirconia was carried out by reverse-strike coprecipitation method followed by drying and calcination of the coprecipitated mass at temperatures that is, 100°C to 500˚C. Precursor solutions of 0.5 M zirconium oxychloride were prepared in double distilled water using magnetic stirrer. Yttrium nitrate solution was also prepared. Zirconium and yttrium-containing precursor solution was prepared by adding an appropriate amount of yttrium nitrate solution to zirconium oxychloride solution to achieve 3 mol% yttria with zirconia in the calcined mass. The prepared precursor solution was added drop wise into a continuously stirred ammonia solution ensuring the pH remained above 10 till complete addition of precursor solution to ammonia. Stirring was continued for 2 h after complete addition of precursor solution into ammonia. The precipitate was left overnight to settle (~12 h) and then filtered on fabric cloth for the removal of excess ammonia. This precipitate was subjected to washing with distilled water by addition of measured quantity of water and stirring for 30 min. The precipitate was left to settle for 3 h and then filtered on fabric cloth. The washing procedure was repeated seven times till $Cl^-$ ion was completely removed from the precipitate. The absence of $Cl^-$ ion was confirmed by absence of AgCl precipitate up on addition of 0.1 N $AgNO_3$ solution to the filtrate.Water-washed precipitate was divided into seven parts.One part was taken as it is and the crystalline powder obtained on its calcination is referred to as waterwashed powder. The other six parts of the precipitate were washed with different amounts of propanol. Quantity of propanol was chosen in reference to the quantity of water present in the precipitate. Water associated with the washed and filtered coprecipitated mass was determined by drying known quantity of coprecipitated mass at 100°C. Following the last wash and after having been kept on the filter cloth for 12 h, the amount of water in the precipitate was reproducibly seen to be around 93% of the filtered coprecipitated mass(Figure 4). During washing and filtration of the precipitate the conditions in the entire study were maintained such that greater than 90% water was retained in the precipitate to facilitate its mixing in propanol and displacement of water with propanol.Propanol amount used for washing the precipitate was varied in the ratio of 1:1, 1:2, 1:3, 1:4, and 1:5 (water: propanol) with respect to the water associated with the precipitate and calcined at temperatures 100˚C,200˚C,300˚C,400˚C and 500˚C(Figure 5)

Figure 4:Water washed Precipitate dried at 100˚C

Figure 5:Different amounts of water to propanol ratio(1:1,1:2,1:3,1:4 and 1:5)

The precipitate was washed with each of the propanol amount twice followed by drying at 100°C. The dried precipitate was calcined at 200°C ,300°C ,400˚C and 500˚C separately for each of the powders washed with different propanol amounts. In the remaining text, zirconium hydroxide precipitate refers to the precipitate with composition expected to yield crystalline 3 mol% yttria stabilized zirconia (3YSZ) upon calcination. Also, water-washed precipitate refers to chloride-free precipitate. Water-washed and propanol-washed powders refer to crystalline YSZ powder obtained by calcination of water-washed and propanol-washed precipitate.
It must be noted that all different characterization tools described below were applied to powders calcined at 100°C,400˚C and 500˚C for CHN analysis (Elementar Vario EL III Model;STIC Cochin) which was used to analyze carbon and hydrogen content in washed and dried precipitate. BET-specific surface area measurements () were carried out for washed and dried precipitates and for powders calcined at 100°C,200˚C,300˚C,400˚C and 500°C, XRD for phase analysis(Bruker AXS D8 Advance; 360° angle range; Vertical, Theta/2 Theta geometry configuration & emperature attachment Anton Paar, TTK 450 model; -170 °C to +450 °C temperature range;STIC Cochin), and Transmission Electron Microscopy (Jeol/JEM 2100; :$LaB_6$ Source; 200kVoltage;Magnification-2000X – 1500000 X;Resolution-Point: 0.23nm, Lattice: 0.14 nm;STIC Cochin ) were used to observe nanoparticulate size, morphology and agglomeration state & FTIR(Fourier Transformer Infrared Spectroscopy of Perkin Elmer,Dimensions: 450*300*210mm(W*D*H),450*300*300mm with UATR installed,Operating temperature range: 0˚C to 50˚C,Storage Temperature: -20˚C to 60˚C,Maximum relative humidity: 80%(non-condensing)with KBr windows,90%(non-condensing)with ZnSe windows:PDACE Kalaburagi) is an analytical technique used to identify organic, polymeric, and in some cases, inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties.

**3.Results & Discussion:**

**1.CHN Analysis(Carbon,Hydrogen & Nitrogen):** CHN Analyzer is a scientific instrument which can determine the elemental concentrations in a given sample. It is used to measure Carbon (C), Hydrogen (H) and Nitrogen (N). Sample sizes may differ depending on system, but most often in around a few mg. For some sample matrices larger mass is preferred due to sample heterogenicity.

| Sample No | Sample Name | N% | C% | H% | Sample Weight, mg |
|---|---|---|---|---|---|
| 1 | 100 Degree Waterwash PPT | ND | 1.24 | 0.89 | 6.06 |
| 2 | 100 Degree Propanol1-1 | ND | 1.07 | 1.26 | 6.78 |
| 3 | 100 Degree Propanol1-2 | 0.01 | 1.52 | 1.52 | 7.10 |
| 4 | 100 Degree Propanol1-3 | ND | 1.34 | 1.53 | 6.73 |
| 5 | 100 Degree Propanol1-4 | ND | 1.02 | 1.86 | 7.16 |
| 6 | 100 Degree Propanol1-5 | ND | 1.18 | 1.67 | 6.71 |

**2.XRD Analysis(X-ray Diffraction):** X-ray powder diffraction (XRD) is a rapid

analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized, and average bulk composition is determined.The Phase is of Face Centered Cubic(FCC).All the 3mol% YSZ samples prepared in the study predominantly are of Miller indices as shown in figure 6 below:For Propanol 1:1,1:2,1:3,1:4 & 1:5 ratio precipitate at 400˚C:(a) (1 1 1),(2 0 0),(2 2 0) & (3 1 1),(b)(1 1 1),(2 0 0),(2 2 0) & (3 1 1),(c)(1 1 1),(2 0 0),(2 2 0) & (3 1 1),(d)(1 1 1),(2 0 0),(2 2 0) & (3 1 1),(e)(1 1 1) & (2 2 0), This miller indices pertains to Cubic 3YSZ structure. For Propanol 1:1,1:2,1:3,1:4 & 1:5 ratio precipitate at 500˚C figure 7 below:(a) (1 1 1),(2 0 0),(2 2 0), (3 1 1)&(2 2 2)(b)(1 1 1),(2 0 0),(2 2 0) ,(3 1 1) & (2 2 2),(c)(1 1 1),(2 0 0),(2 2 0) ,(3 1 1)&(2 2 2),(d)(1 1 1),(2 0 0),(2 2 0) (3 1 1)&(2 2 2),(e)(1 1 1),(2 0 0), (2 2 0) & (3 1 1).This miller indices pertains to Cubic 3YSZ structure.
Crystallite Size for Propanol washed at 400˚C (a)1:1 ratio=1.37488nm,1.48638nm,1.24530nm & 1.22800nm(b)1:2 ratio=1.3745nm,1.409nm & 1.30424nm(c)1:3 ratio=1.39979nm,1.4133nm,1.2181nm & 1.248nm(d)1:4 ratio=1.5614nm,1.40070nm,1.2928nm & 1.2976nm.
Crystallite Size for Propanol washed at 500˚C(a)1:1 ratio=1.5100nm,1.54459nm,1.38026nm,1.42332nm & 1.5545nm(b)1:2 ratio=1.4799nm,1.4309nm,1.6481nm & 1.64515nm(c)1:3 ratio=1.4772nm,1.4346nm,1.6339nm & 1.6345nm(d)1:4 ratio=1.3202nm,1.29052nm,1.5570nm & 1.4875nm(e)1:5 ratio=1.3060nm,1.2530nm,1.5036nm & 1.4646nm.

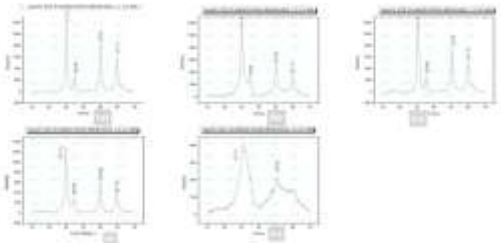

Figure 6: XRD patterns for 3YSZ nanocrystalline powders produced by Propanol washing with 1:1, 1:2,1:3,1:4 & 1:.5 (water to propanol ratio) that were calcined at 400˚C

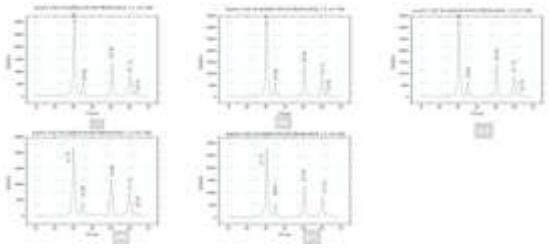

Figure 7: XRD patterns for 3YSZ nanocrystalline powders produced by Propanol washing with 1:1,1:2,1:3,1:4 & 1:.5 (water to propanol ratio) that were calcined at 500˚C

**3.TEM Analysis(Transmission Electron Microscope):**TEM were used to observe nanoparticulate size, morphology and agglomeration state. The TEM micrographs showed that the size of the primary particles was in the range of 100-1 nm(Figure 8,Figure 9 & Figure 10) .

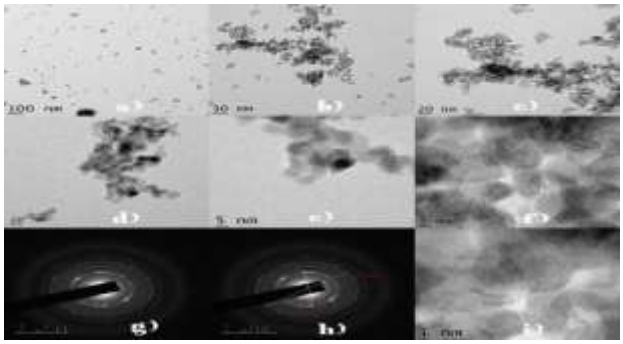

Figure 8:TEM analysis of Propanol 1:2 ratio Precipitate

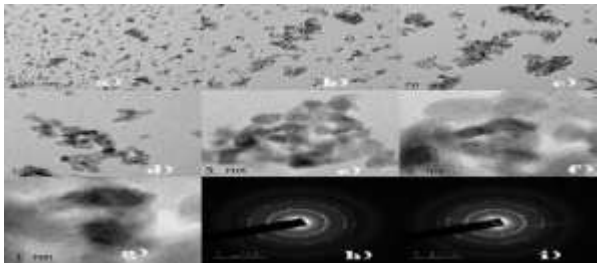

Figure 9:TEM analysis of Propanol 1:3 ratio Precipitate

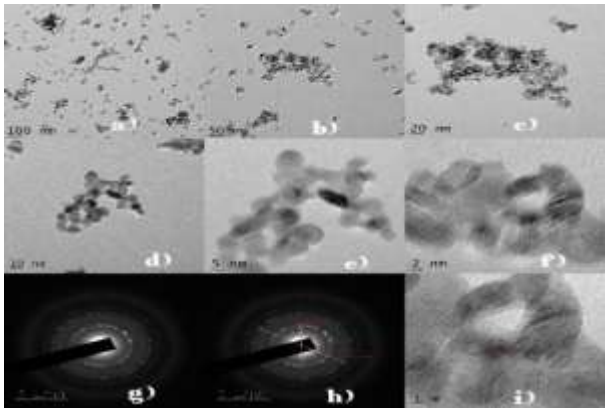

Figure 10:TEM analysis Propanol 1:4 ratio Precipitate

**4.FTIR (Fourier Transform Infrared Spectroscopy)Analysis**:FTIR spectra of 3mol% YSZ washing with Propanol at 100˚C & 500˚C.The graphs shown in figure 11 & 12 shows about organic & inorganic compounds such as at 2932,2883,1466,1408,816 & 638 shows the bonds of the precipitate washed with Propanol(C-H bond,C=$CH_3$+C=C bond,Zr-OH bond & Zr-O-Zr bond)

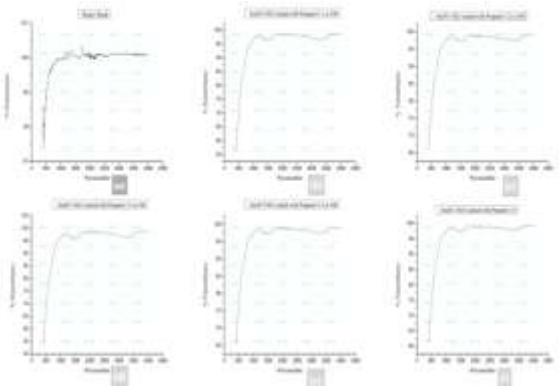

Figure 11 :FTIR Graphs of 3mol% YSZ washed with propanol at 100˚C (a)Water Wash,(b)1:1 ratio,(c)1:2 ratio,(d)1:4 ratio & (e)1:5 ratio

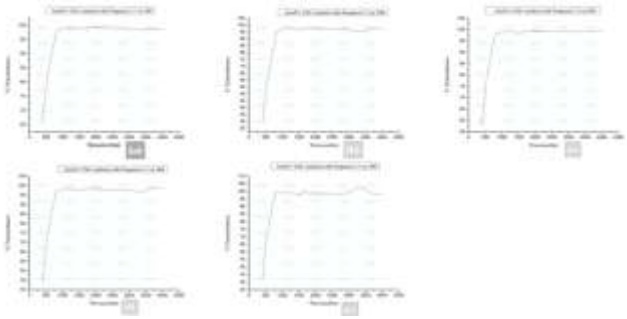

Figure 12 :FTIR Graphs of 3mol% YSZ washed with propanol at 500˚C(a)Water Wash,(b)1:1 ratio,(c)1:2 ratio,(d)1:4 ratio & (e)1:5 ratio

**Conclusion & Future scope**

Deagglomeration attained in calcined nano YSZ powders improved with increase in amount of propanol used for washing of the yttrium–zirconium hydroxide precipitate. Presence of adsorbed propanol on the yttrium–zirconium hydroxide was confirmed through CHN,XRD, TEM,FTIR & BET.The water present in the precipitate was required to reduce extent of agglomeration considerably in the calcined powders at 100˚C,200˚C,300˚C,400˚C & 500˚C are studied.The CHN analysis showed the

C%,H% & N% in the nanopowders ,it is the most essential - and in many cases the only - investigation performed to characterize and/or prove the elemental composition of an organic sample. Numerous compounds include no additional elements besides C, H and N except oxygen, which is seldom determined separately.From the results it shows that the samples are of organic in nature.XRD study showed that the samples are of Face Centered Cubic shape as with of JCPDS(Joint Committee of Powder Diffraction Society) in with respective Miller indices & Crystallite Size, ,TEM results showed the morphology of Zirconia nanoparticles with respect to Agglomeration state of nanoparticles.FTIR Results showed the presence of organic compounds present in samples.

This can be further used in future for making compacts & sintering at 900˚C,1300˚C & 1400˚C with soaking time -2h & Sintering time-30minutes.Further the composites can also be prepared & the results such as Tensile,Impact,Hardness,Wear Studies can be carried out.

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