

## TO EVALUATE THE APPLICABILITY OF ALKOXIDE SOL-GEL METHOD IN SYNTHESIS OF YSZ NANOPOWDER THROUGH APPROPRIATE HYDROLYSIS ROUTE

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**Abstract:** Synthesis of YSZ nanopowder by alkoxide sol-gel method, through two different hydrolysis routes, one under careful control by using acetylacetonone as ligand, and the other through basic hydrolysis, was investigated. The synthesized powders were characterized by various analytical techniques such as, XRD, STA, PSA, BET, SEM, and TEM. The results showed that, the YSZ powders prepared through the basic hydrolysis route consist of weakly agglomerated nanosized spherical particles; whereas the products obtained through the controlled hydrolysis route, consist of hard irregular shaped agglomerates. Sinterability of these powders was examined at 1480 °C, which showed that the powder synthesized through the basic hydrolysis route attains a density of 94%, against 60% for the other case. It was therefore concluded that, alkoxide sol-gel method through basic hydrolysis route, can be more suitable for the synthesis of YSZ nanopowder and its subsequent sintering.

**Keywords:** Yttria-stabilized zirconia, sol gel, alkoxide, hydrolysis, sintering

### 1. INTRODUCTION

Zirconia-based ceramics, due to their specific mechanical properties, have attracted attention of many investigators in attempts to develop their application fields. In fact, suitable combination of fracture toughness and strength can bring about the desired properties for these ceramic materials. Commercial applications of ZrO<sub>2</sub>-based materials include femoral ball heads, dental restoratives, extrusion dies and cutting tool inserts, seals, thrust bearings, valve seats, valve guides for turbocharger rotors, pump parts, knives and scissors used in paper industries, diesel engine parts, roller guide, bearings in seal-less pumps, magnetic drives, seal faces and milling media[1]. Polycrystalline tetragonal zirconia (TZP) is a material with nearly 100% t-ZrO<sub>2</sub> phase, stabilized by additions of yttria or ceria. 3YSZ has been considered significantly as a structural ceramic material, requiring a dense and fine-grained microstructure.

YSZ powders are commonly prepared by conventional routes such as solid state reactions and thermal decomposition. In these types of processes, intensive mixing of reactants and calcinations at high temperatures for long times

are necessary. Due to the long thermal treatment, the as-synthesized powders lose their reactivity and at the same time, size and morphology of the particles cannot be appropriately controlled. In order to overcome these difficulties, various soft chemical processes like, sol-gel, co-precipitation, freeze drying and hydrothermal have been investigated [2]. Both freeze drying and hydrothermal processes are not commonly employed due to the complexities which may be encountered during the powder production. Co-precipitation and sol-gel processes can be therefore, considered as the alternate choices for the ceramic powder production. The powders obtained by co-precipitation techniques are often highly agglomerated in nature which consequently could affect the sinterability and mechanical properties of the final product. Finally, sol-gel has proved to be as an appropriate procedure for this purpose, since the components can be readily mixed in the molecular scale to make high purity and homogenous powders together with the proper control over size and morphology. It therefore, seems to be a promising process for producing fine uniform particles with low agglomeration [3]. However, being a solution based technique, careful control over the

processing parameters is necessary without which, high quality powders with reproducibility cannot be easily produced. This may be the main reason for its limited applications in manufacturing of certain ceramic materials.

Most of the reported sol-gel methods for preparation of zirconia-based materials are based on the aqueous media, using inorganic precursors. For instance, manufacturing of sinterable zirconia powder has been already achieved through sol-gel processing routes, using zirconyl nitrate and  $ZrCl_4$  precursors in aqueous solution [4, 5]. Although, the aqueous sol-gel methods are easy and cost effective, their final products are more prone to agglomeration, as compared to the alkoxide sol-gel methods. Furthermore, the hydrolysis and condensation processes in alkoxide sol-gel methods can be controlled in such a way as to tune the size and morphology of the particles, as well as their structural characteristics. However, care should be taken during the synthesis process, as zirconium alkoxides undergo a severe hydrolysis in the presence of water.

Some investigators have synthesized the stabilized zirconia powders using alkoxide precursors, emphasizing on the controlled textural and structural characteristics of the prepared powders [6-10].

However, production of dense materials from the synthesized zirconia powders and the examination of their properties, have not been reported much.

Caruso 'et al' [11] prepared  $ZrO_2$  powders using the solutions of zirconium n-propoxide (ZNP) in various alcohols. The results showed that the kind of alcohol does not influence the properties of the powders. However, pH of the medium used in the hydrolysis process, strongly affects the microstructure, morphology and sintering process of the prepared samples. In fact, the powder synthesized at pH 5 could result in higher densification and hardness values after sintering.

Wen [12] prepared Ytria-stabilized zirconia (YSZ) powders by basic hydrolysis of a solution containing zirconium isopropoxide and yttrium nitrate. Crystallization of cubic YSZ occurred at temperatures near to 450 °C K, yielding ceramic powders with high specific surface areas, the values of which depended on the hydrolysis conditions.

Sintering of the synthesized powder at 1420 could yield ceramics with nearly theoretical density and homogeneous grain size distribution. Zevret 'et al' [13] prepared ultra-fine grained  $Y_2O_3$  doped  $ZrO_2$  ceramic powders by two different hydrous gel precipitation techniques, the hydrolysis of metal alkoxides and metal chlorides. The ceramic powders prepared by the hydrolysis of metal alkoxides consisted of relatively weak, irregular shapes and porous agglomerates. The powders prepared by hydrolysis of the metal chloride solution consisted of stronger, more regular shapes and denser agglomerates. Mamana 'et al' [14] synthesized YSZ powders by alkoxide sol-gel method at pHs 0.5 and 5 (acidified by  $HNO_3$ ) with or without acetic acid in the hydrolysis medium. It was found that the compacts prepared from the YSZ powders obtained at pH 5, without acetic acid, exhibits the greatest sinterability.

It is well known that, by the use of certain complexing agents in alkoxide sol-gel methods, it is possible to control the hydrolysis rate of zirconium alkoxides, in attempts to control the size and morphology of the synthesized particles. Acetylacetone has been so far used in several investigations for this purpose, especially for the fabrication of zirconia-based ceramics as coatings materials. However, its effect on the structural characteristics of the synthesized YSZ powders, as well as the sintered samples, have rarely been studied.

In the present research work, an attempt was therefore made, in order to evaluate the influence of the hydrolysis conditions on the characteristics of the synthesized YSZ powder by sol-gel processing. To do this, controlled hydrolysis process by using acetylacetone at mild acidic pH (5-6), and also hydrolysis at basic pH (10-11), without special control over the hydrolysis process, have been carried out. Finally, the sinterability of the synthesized powders by the two mentioned sol-gel routes was examined.

## 2. EXPERIMENTAL

### 2.1. Powder Preparation

Zirconium propoxide (Sigma-Aldrich), Yttrium (III) nitrate hexahydrate (99.8%, Sigma-Aldrich), 1-propanol (99.8%, Merck), acetylacetone (>99%,

Merck) ammonia solution 25% (>99.8%, Merck) were used as the starting materials.

The flowchart showing the procedures used for the preparation of YSZ powders, is presented in Fig. 1. The hydrolysis process was carried out through two different routes; the first one by using acetylaceton (AcAc) along with zirconium alkoxide and yttrium nitrate in an alcoholic solution with controlled addition of water, in order to control the hydrolysis rate, and the second one by controlled addition of ammonia solution to the same solution mixture, but without AcAc. The molar ratios for the reactants, propanol: H<sub>2</sub>O: AcAc: Zr were taken as, 50:7:0.3:1 AcAc was initially dissolved in

propanol and stirred for 10 min, after which zirconium alkoxide was added and stirred for another 10 min., then the required amount of yttrium nitrate corresponding to 3% mol Y<sub>2</sub>O<sub>3</sub> was dissolved in propanol and added to the above mixture. Finally, distilled water or ammonia solution was slowly dripped to the reacting mixtures. The products of the above processes were dried at about 50 °C under air for 24 hours and then calcined.

## 2. 2. Characterization

Characteristics of the powders were determined by various analytical techniques such

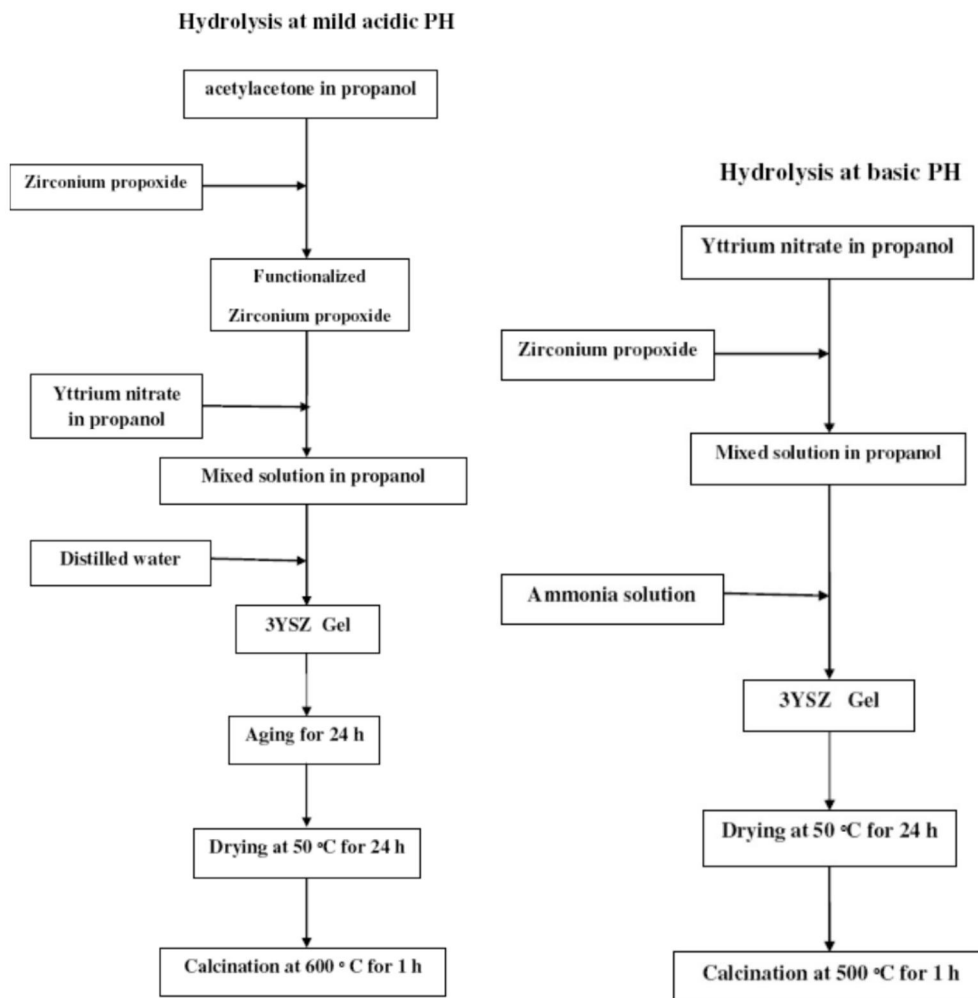


Fig. 1. Flowchart of the procedures used for the preparation of 3YSZ powder via sol gel method.

as, thermal analysis, DTA/TGA (STA 1500, Rheometric Scientific,uk) under air with heating rate of 10 °C/min, particle size analysis by laser method (Fritsch, Germany), BET (Belsorp, Japan), SEM (Philips, XL30, Netherland) and TEM (Philips, EM208S,Netherland).

In order to evaluate the sinterability of the synthesized powders, they were initially pressed into pellets using steel die with 10 mm diameter under a pressure of 350 Mpa and then sintered at temperature of 1480 °C for 2 hours. The sintered samples were characterized by XRD (Philips, PW 1800, Cuka, Netherland) and SEM analytical techniques. Densities of the pellets were measured by Archimedes' method.

### 3. RESULTS AND DISCUSSION

The YSZ powders, which synthesized through two different hydrolysis routes, i.e. one through the controlled hydrolysis process by using acetylacetonate as complexing agent and the other through a basic hydrolysis using ammonia, were named as samples A and B respectively. Fig. 2 shows the result for the thermal analysis (TGA and DTA curves) of the sample A. Considering the TGA and the DTA curves, various steps of the

weight losses as well as the various reactions occurred can be observed, which correspond to the removal of water and alcohol (up to ~100 °C), decomposition and removal of various organic and inorganic compounds like acetylacetonates, alkyl groups, hydroxyls, nitrates and etc., along with the corresponding endothermic and exothermic reactions (up to ~550 °C), including the tetragonal phase crystallization occurring at ~490 °C. As the DTA curve shows, calcination of the sample A completes at ~600 °C. In the same way, Fig. 3 shows the result of the thermal analysis for the sample B. It can be observed that, the trends of the weight losses for both the samples look almost similar. However, in the case of sample B, the DTA curve shows that the exothermic reactions corresponding to the burning of organic groups and crystallization of the tetragonal phase occurred at about 300 °C and 450 °C, respectively. Calcination temperature of the sample B was therefore, selected at about 500 °C.

The powders characteristics are presented in table 1. Although, it is observed that the particle/agglomerate size distributions are almost the same for the samples A and B, appreciable difference in their surface areas clearly indicates that, in the case of the sample B soft

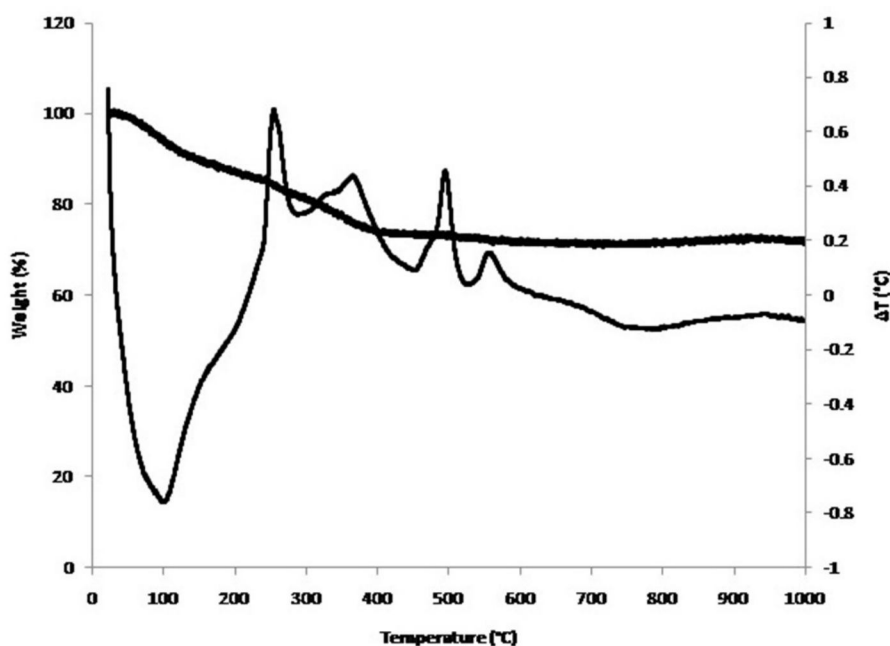


Fig. 2. Thermal analysis curve of powder type A

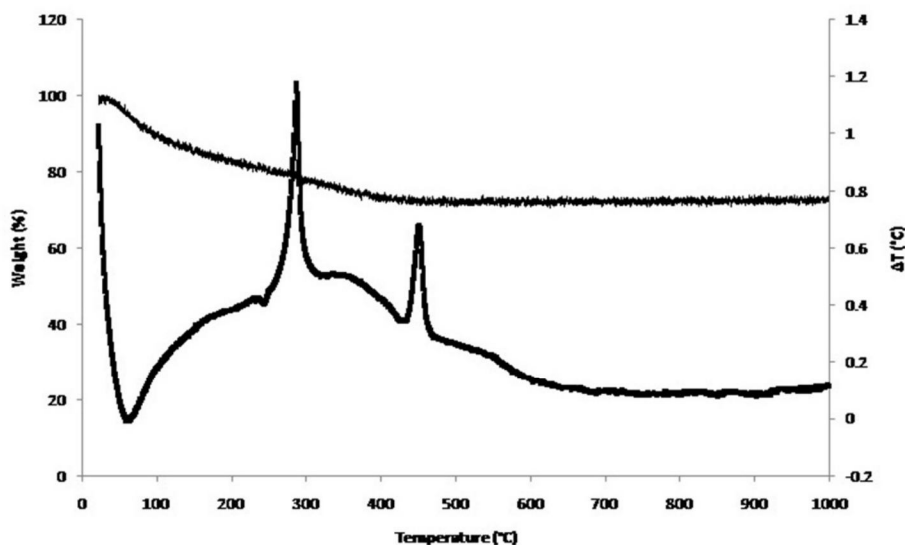


Fig. 3. thermal analysis curve of powder type B

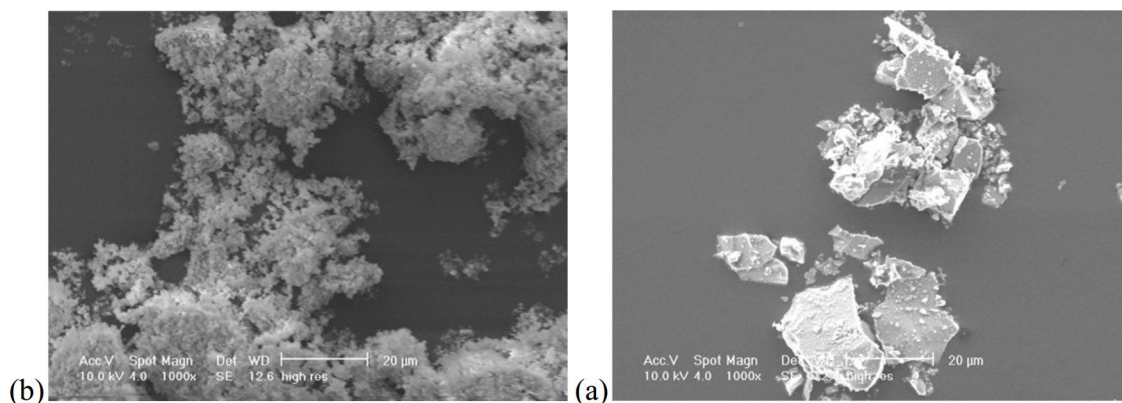
Table 1. Powder characteristics of sample A and B

particle/agglomerate size distribution( $\mu\text{m}$ )			surface ( $\text{m}^2/\text{gr}$ ) area	Crystallite size (nm)	phase	Powder type
D <sub>90</sub>	D <sub>50</sub>	D <sub>10</sub>				
30.9	10.9	1.08	1.9	55	100% tetragonal	A
28.9	9.6	0.995	87.1	32	100% tetragonal	B

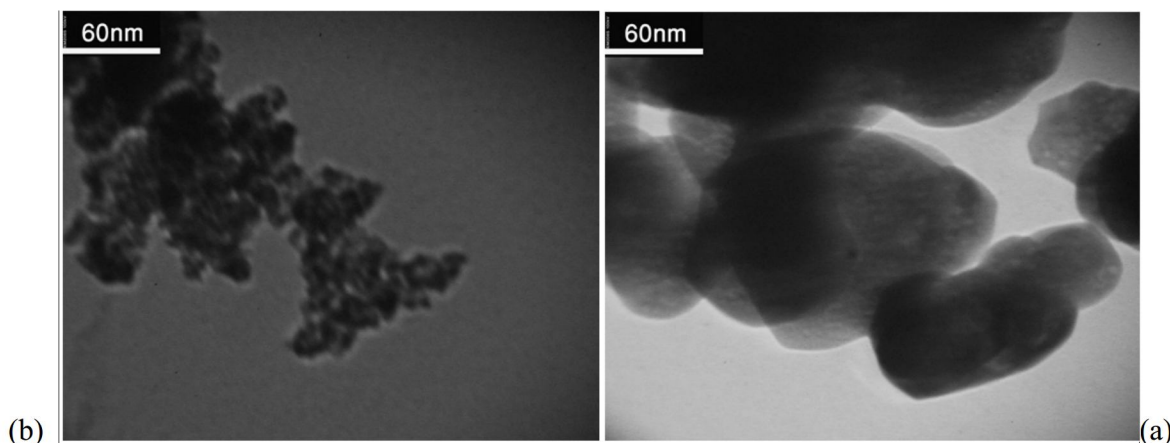
agglomeration could exist, in contrast to the sample A. In fact, BET surface area obtained for the sample B clearly indicates that the particles are in nanosized range, whereas in the case of the sample a, particles become much coarser as a result of the formation of hard agglomerates during the calcinations process.

SEM micrographs of the samples A and B are shown in figures (4-a) and (4-b) respectively. It can be observed that the sample A consists of large particles with irregular shapes, while in the case of the sample B, almost spherical nanosized particles can be observed. TEM image shown in Fig. 5 also clearly indicates the formation of soft agglomerates consisting of nanosized particles in the case of sample B, in contrast to the sample A

which contains quite larger particles. It can be therefore concluded that, in spite of implying a better control over the hydrolysis process by using an appropriate complexing agent like acetylacetone, the quality of the powder produced through this route is much lower as compared to the powder prepared through the simple basic hydrolysis. Obtaining of this result may be attributed to the nature of the formed primary particles and their surface structure, which may determine the extent and strength of the interactions between them, which in turn influence the degree of agglomeration. Similar behavior could also be observed by other investigators who studied the effect of pH on the hydrolysis process [11, 13 and 14]. According to



**Fig. 4.** SEM micrographs of the synthesized zirconia powders (a): sample A (b): sample B



**Fig. 5.** TEM micrographs of the synthesized zirconia powders (a): sample A (b): sample B

them, the presence of  $H^+$  ions reduce the hydrolysis rate and condensation takes place by the alcoxolation mechanism; under these conditions the precursor gel was developed by the cluster-cluster, rather than the monomer-cluster growth process and therefore, synthesized powder comprised large particles and hard agglomerates [14]. Also it cited that at slightly acidic pH, a part of the precipitated yttria in the gel may dissolve and reprecipitate at the point of contact between gel particles. This may increase the formation of necks between the gel particles, which consequently results in a rather strong aggregate during the calcination process [13].

In order to evaluate further the characteristics of the sol-gel derived powders through the

different hydrolysis routes, their sinterability were examined according to the described procedures in the experimental section. The green densities of the pressed powders for the samples A and B were found to be 55 and 43% of the theoretical density, respectively. The appreciable difference between these values may be related to the size and shape of the particles or agglomerates, as well as their porosity. After sintering process, the densities were found to be 60 and 94% for the samples A and B, respectively. This result clearly indicates the suitability of powder B for use in fabrication of the sintered YSZ materials, a property dependent on the powder characteristics such as particle size and morphology as well as their homogeneity.

X-ray diffraction patterns of the sintered

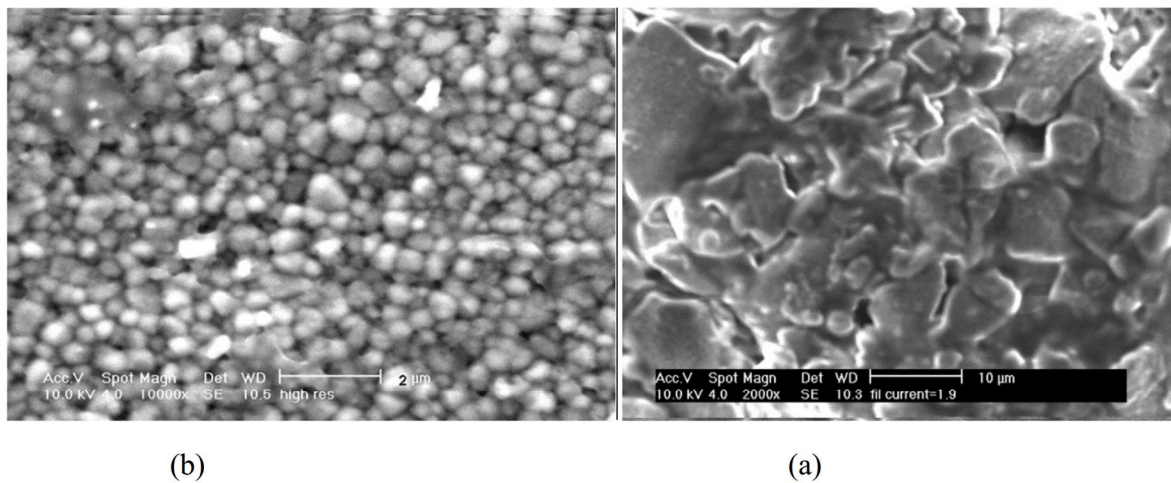


Fig. 6. SEM micrographs of the sintering products of powder samples (a): A and (b): B

samples A and B presented in fig. 7, indicate the formation of pure stabilized tetragonal zirconia phases for both the cases. However, the higher peaks intensities obtained in the case of the sample A, indicates the formation of larger crystallites for this sample.

SEM images of the samples A and B after sintering are shown in figures (6-a) and (6-b) respectively. Observed particle size and morphology of the samples clearly explains their measured density values. In fact, submicron

grains and their homogeneity in size and morphology observed in the case of the sintered sample B may indicate its superior microstructure, giving rise to better mechanical properties.

#### 4. CONCLUSION

The experimental results obtained in the present research work indicate that, through the basic hydrolysis route, the alkoxide sol-gel

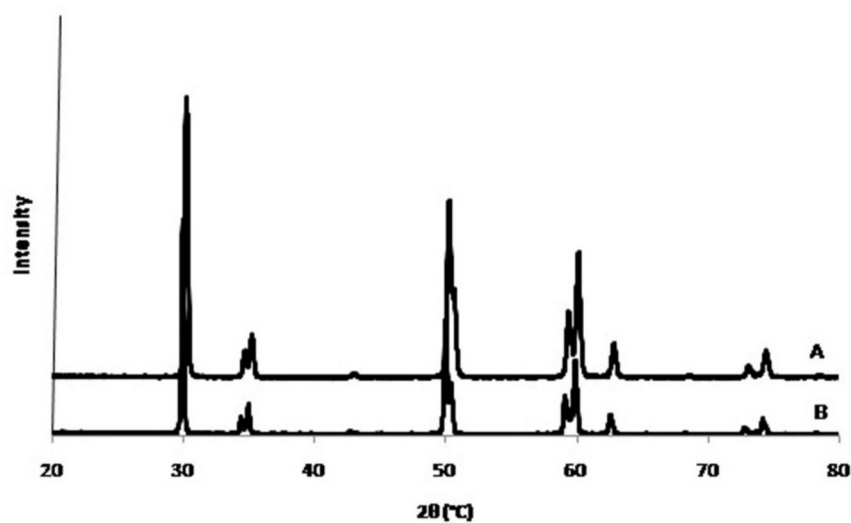


Fig. 7. X-ray diffraction patterns of the sintered samples (a): A and (b): B

method can be efficiently used for the synthesis of YSZ nanopowders, as well as the fabrication of its bulk materials. YSZ powder synthesized through carefully controlled hydrolysis route by using acetylacetone as ligand, consisted of hard agglomerates, which results in its poor sinterability.

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