

## Araştırma Makalesi / Research Article

**Synthesis of Yttria-Stabilized Zirconia (YSZ) Ceramic Powder Using Modified Sol-Gel Method****\*Aysu AYDINOĞLU, Afife Binnaz HAZAR YORUÇ**<sup>1</sup>Yıldız Technical University, Department of Metallurgical and Materials Engineering, 34210, Istanbul, Turkey.\* Corresponding author e-posta: aysukarakas@gmail.com ORCID ID: http://orcid.org/0000-0002-1875-2249  
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**Abstract**

Zirconia is widely used ceramic powders as a biomaterial in medical applications due to its similarity with tooth color, good mechanical and bioinert properties. Its high temperature forms can be fully or partially stabilized by the addition of oxides such as MgO, CaO and Y<sub>2</sub>O<sub>3</sub>. Recently, yttria stabilized zirconia has been mostly studied because of its lots of advantages. In this study, 3% mol and 8% mol yttria stabilized zirconia powders have been synthesized using a simple sol-gel process. ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O and Y(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O was dissolved in ethylene glycol and pure water, respectively and mixed together. After mixing pH was adjusted to 3.5 using HNO<sub>3</sub>. Final suspension was stirred until it becomes homogenized. Homogeneous mixture dried at 120°C and then sintered at 1200°C. Crystallite sizes and mineralogical composition were determined by XRD. Surface area was measured by BET method and particle size was calculated. Density of powders was measured by ultrapicnometre. Also, morphological structure was examined by SEM. Tetragonal ZrO<sub>2</sub> and tetragonal ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> phases were observed. Current studies showed that YSZ powder can be effectively synthesis with the present method.

**Keywords**

Yttria-stabilized zirconia; Tetragonal zirconia powder; Stabilization; Sol-gel

**Modifiye Sol-Jel Yöntemi Kullanılarak İttriya Katkılı Zirkonya Sentezi****Öz**

Zirkonya, tıbbi uygulamalarda, diş rengine benzerliği, iyi mekanik ve biyoinert özellikleri nedeniyle yaygın olarak kullanılan seramik tozlarıdır. Yüksek sıcaklık formları MgO, CaO ve Y<sub>2</sub>O<sub>3</sub> gibi oksitlerin eklenmesi ile tamamen veya kısmen dengelenebilir. Son zamanlarda, itriya stabilize zirkonya çoğunlukla avantajları nedeniyle incelenmiştir. Bu çalışmada, basit bir sol-jel işlemi kullanılarak %3 mol ve %8 mol itriya stabilize zirkonya tozları sentezlenmiştir. ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O ve Y(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O sırası ile etilen glikol ve saf su içerisinde çözündürüldü ve karıştırıldı. Karıştırmanın ardından pH, HNO<sub>3</sub> ile 3.5'e ayarlandı. Elde edilen süspansiyon homojen hale gelinceye kadar karıştırıldı. Homojen karışım, 120°C'de kurutuldu ve daha sonra 1200°C'de sinterlendi. Elde edilen tozların kristal boyutları ve mineralojik kompozisyon XRD ile belirlenmiştir. Yüzey alanı BET metodu ile ölçülmüş ve partikül büyüklüğü hesaplanmıştır. Tozların yoğunluğu ise ultrapiknometre ile ölçülmüştür. Ayrıca SEM ile morfolojik yapı incelenmiştir. Tetragonal ZrO<sub>2</sub> ve tetragonal ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> fazları gözlemlendi. Mevcut çalışmalar, YSZ tozunun bu yöntemle etkili bir şekilde sentezlenebileceğini göstermektedir.

**Anahtar kelimeler**

İttriya stabilize zirkonya; Tetragonal zirkonya; Stabilizasyon; Sol-jel.

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**1. Introduction**

Zirconia is a crystalline dioxide form of zirconium (Manicone et al. 2007). Its properties such as excellent mechanical strength and toughness, good chemical and dimensional stability, opacity and similarity to tooth color make it an attractive ceramic biomaterial (Manicone et al. 2007; Piconi

and Maccauro 1999). Zirconia has three crystallographic forms depending on the temperature (Denry and Kelly 2008). Pure zirconia is monoclinic phases at room temperature up to 1170°C, tetragonal phase between 1170°C and 2370°C and cubic phase at above 2370°C up to the

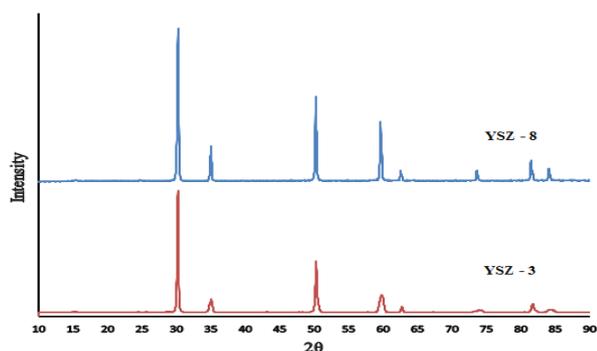
melting point (Denry and Kelly 2008; Kelly and Denry 2008). However, the tetragonal phase (t) is tend to transform monoclinic phase (m) during cooling. This transformation causes volume expansion of about 3-4 v.% (Pilathadka et al. 2007) and lead to catastrophic failure. To avoid phase transformation, stabilizing oxides such as CaO, MgO, Y<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> are added for retention the tetragonal structure at room temperature and to control t-m transformation (Denry and Kelly 2008). Stabilized cubic and tetragonal forms have a common usage and importance due to their good mechanical properties, oxygen conductivity, thermal stability and chemical resistance (Ray et al. 2000). Recently, the most preferred material among these oxides is yttria partially-stabilized zirconia (Y-PSZ) (Kaya 2013) especially in dental restorations instead of metallic dental restorations because of its biocompatibility and natural appearance (Hsu et al. 2011). Fully stabilized zirconia has tetragonal ZrO<sub>2</sub> poly-crystals (Y-TZP). However, partially stabilized zirconia (Y-PSZ) has both the monoclinic and tetragonal phases in matrix (Hsu et al. 2011). Doping of Y-TZP and Y-PSZ with 3-5% mol Y<sub>2</sub>O<sub>3</sub> gives it excellent mechanical properties such as fracture toughness and strength (Wang et al. 2013). Recently, several processes is reported to synthesis YSZ nano particles such as hydrothermal, co-precipitation, hydrolysis of metal oxides and sol-gel processes (Hsu et al. 2011; Kuo et al. 2005). The sol-gel method has some advantages, such as low sintering temperature, high purity and high degree of homogeneity in molecular scale (Kuo et al. 2005). However preparation of stable zirconia sol using zirconia alkoxide is very difficult and complex process. One of the reasons is the extremely rapid reaction of the zirconia alkoxide with water. Therefore, the synthesis of the zirconia sol needs extreme carefulness, and the preparation is very sensitive to experimental conditions. In this study, gelation step obtained using poly ethylene glycol (PEG) instead of metal alkoxide. Thus, sol-gel technique modified as an effective way to synthesis 3% mol and 8% mol YSZ powder.

## 2. Materials and Methods

Zirconium (IV) oxynitrate hydrate, [ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O, purity %99 was supplied by Sigma-Aldrich, USA] and yttrium (III) nitrate hexahydrate [Y(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O purity %99,8 was supplied by Sigma- Aldrich, USA] were used as starting materials in this study. Firstly, 3M ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O and 1M Y(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O solution was mixed with ethylene glycol (purity ≥ % 99.5 was supplied by Merck, Germany) and deionized water, respectively. Then, Y(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O was added to ZrO(NO<sub>3</sub>)<sub>2</sub>.xH<sub>2</sub>O solution drop by drop and mixed to make YSZ solution. Resulted mixture was stirred and pH was adjusted to 3.5 using HNO<sub>3</sub>. This white and milky mixture was dried at 120°C until they become dark brown. Drying powders were grounded with agat mortar and sintered at 1200°C for 2 hours. Resulted powders were called 3% mol YSZ-3 and, 8% mol YSZ-8. The crystal structure was analyzed by X-ray diffraction (XRD-Rigaku ,Dmax 2200) and crystal size was calculated by Scherrer equation. Morphological structures were characterized using scanning electron microscope (SEM-Tescan, Vega 2). Surface area was measured by BET method (Quantachrome, Quadrasorb SI) to calculate particle size of the powders. Density of powders was measured by ultrapycnometer (Quantachrome, Ultrapyc 1200e).

## 3. Results and Discussion

Fig.1 shows the X-ray diffraction patterns (2θ range between 10° and 90° ) of YSZ-3 and YSZ-8 samples sintered at 1200°C. 2θ of 30.2 (101), 50.3 (112) and 59.7 (103) peaks reveals the characteristics peaks of t-ZrO<sub>2</sub> for YSZ-3 (Piconi and Maccauro 1999). Also, 2θ of 35.0 (110) and 81.7 (213) peaks show the presence of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> phase. On the other hand, 2θ of 30.2 (101), 59.6 (103) and 73.6 (004) peaks of t-ZrO<sub>2</sub> (Piconi and Maccauro 1999) was observed for YSZ-8 besides 2θ of 84.0 (114) of t-ZrO<sub>2</sub>. Also, 35.0 (110), 50.2 (112), 62.5 (202), and 81.5 (213) reveal the peaks of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>. The primary phase of YSZ-3 and YSZ-8 was tetragonal phase. Furthermore, intensity of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> peaks on the 2θ was increased with the Y<sub>2</sub>O<sub>3</sub> content.



**Figure 1.** XRD patterns of YSZ-3 and YSZ-8 powders

The average crystallite sizes of the t-ZrO<sub>2</sub> of YSZ-3 and YSZ-8 powders were calculated by the Scherrer equation (Kuo et al. 2005):

$$D_{XRD} = 0.89\lambda / (B \cdot \cos\theta) \quad (1)$$

where  $D_{XRD}$  is the crystallite size,  $\lambda$  is the wavelength of the X-ray radiation,  $B$  is the width of the diffraction peak measured at half maximum intensity and  $\theta$  is the Bragg angle.

Tab.1 and Tab.2 show the full width at half maximum (FWHM) and crystallite sizes of the main three peaks of samples. According to Eq.1, the crystallite size of powders was determined as 28.62 nm for YSZ-3 and 48.31 nm for YSZ-8. These results show that crystallite size has a tendency to increase as a function of Y<sub>2</sub>O<sub>3</sub> content (Amézaga-Madrid et al. 2012).

The specific surface areas and densities of resulting powders were measured by BET technique and ultrapicnometer, respectively. Tab.3 shows the surface area, and density of samples. Particle size of synthesized powders was calculated using surface area measurements using the following equation (Zhu and Fan 2005):

**Table 1.** The crystallite size of YSZ-3 at 1200°C.

	Peak 1	Peak 2	Peak 3
Obs. Maximum (°)	30.24	50.30	59.78
FWHM (°)	0.207	0.282	0.573
Crystallite size (nm)	39.30	30.77	15.80

The specific surface areas and densities of resulting powders were measured by BET technique and ultrapicnometer, respectively. Tab.3 shows the surface area, and density of samples. Particle size of synthesized powders was calculated using surface area measurements using the following equation (Zhu and Fan 2005):

$$D_{BET} = \frac{6}{\rho \cdot S_{BET}} \quad (2)$$

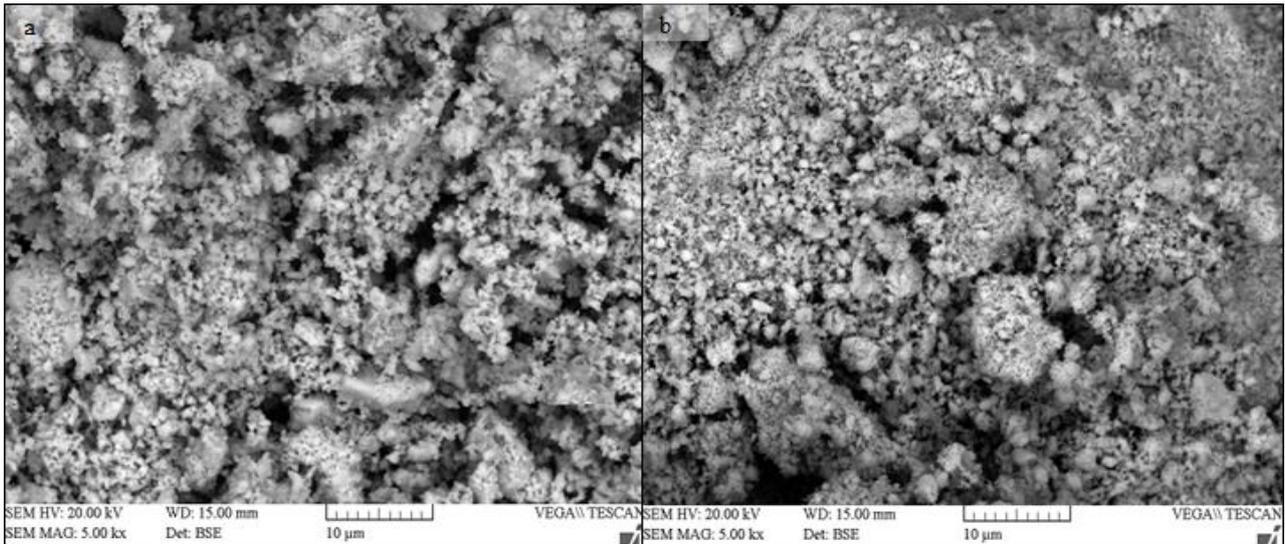
**Table 2.** The crystallite size of YSZ-8 at 1200°C.

	Peak 1	Peak 2	Peak 3
Obs. Maximum (°)	30.26	50.26	59.66
FWHM (°)	0.209	0.170	0.165
Crystallite Size (nm)	39.04	51.02	54.87

$D_{BET}$  is the average particle size,  $S_{BET}$  is the specific surface area expressed in m<sup>2</sup>/g, and  $\rho$  is the theoretical density in g/cm<sup>3</sup>. According to measurements, particle size of YSZ-3 is 338.43 nm while particle size of YSZ-8 is 155.53 nm. The difference between particle size and crystallite size are due to higher agglomeration of particles. This physical agglomeration of crystallites is associated with higher surface energy of smaller crystallites (Kelly and Denry 2008).

When Y<sup>+3</sup> is doped into the ZrO<sub>2</sub> lattice, oxygen vacancies are created to sustain local electrical neutrality. The oxygen vacancies reduce the effective coordination number of Zr<sup>+4</sup> cations below 7 due to their tendency to associate with Zr<sup>+4</sup>. The presence of large numbers of oxygen vacancies on grain surface by doping of Y<sup>+3</sup> and nano-size effect increase the surface energy drastically and reduce the growth activation energy of nanoparticles (Chen et al. 2004). According to this approach Tab.1 shows decreasing of particle sizes and increasing surface area by the addition of Y<sub>2</sub>O<sub>3</sub> to ZrO<sub>2</sub>. Also, density of particles tends to increase by Y<sub>2</sub>O<sub>3</sub> content.

Fig.2 shows the SEM images of the samples sintered at 1200°C. In these cases, large agglomerations were observed for both YSZ-3 and YSZ-8 powders. The most common problem in conventional nano-



**Figure 2.** SEM images of (a) YSZ-3 and (b) YSZ-8

powders is solid-state bonds formed between nanoparticles (Kuo et al. 2005). Agglomeration tendency of YSZ-3 and YSZ-8 can be easily understood with this aspect.

**Table 3.** Density, surface area and particle size values of YSZ-3 and YSZ-8

	Density (g/cm <sup>3</sup> )	Surface area (m <sup>2</sup> /g)	Particle size (nm)
YSZ-3	6.01	2.945	338.43
YSZ-8	6.40	6.408	155.53

#### 4. Conclusion

3% mol yttria stabilized zirconia (YSZ-3) and 8% mol yttria stabilized zirconia (YSZ-8) powders has been synthesized using sol-gel method at the acidic pH and with the 1200°C sintering temperature. The results have shown the reproducibility of YSZ using ethylene glycol. The XRD patterns verified pure t-ZrO<sub>2</sub> formation. Intensity of YSZ-8 peaks was higher than YSZ-3. The crystallite sizes of the samples are 28.62 nm for YSZ-3 and 48.31 nm for YSZ-8. Higher Y<sub>2</sub>O<sub>3</sub> content in the structure caused increase of the crystallite size of YSZ-8 powders. The specific surface area of the powders was measured using the BET method (2.945 m<sup>2</sup>/g for YSZ-3 and 6.408 m<sup>2</sup>/g for YSZ-8) and the particle sizes were calculated corresponding to surface areas (338.43 nm for YSZ-3 and 155.53 nm for YSZ-8). Also agglomeration of

the samples was evaluated by SEM examinations. As a result, this study proved that tetragonal YSZ powders could be effectively and easily synthesis at acidic pH and 1200°C by modified sol-gel method without any transformation to monoclinic phase.

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