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Research paper

Characterization of Zirconia- Hydroxyapatite Nanocomposites for Orthopedic and Dental Applications

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Abstract

Zirconium oxide ceramic was proposed for different biomedical applications. It is used in orthopedic as hip and knee prostheses and in dentistry due to the good mechanical, biological high corrosion and wear resistance properties, addition to the aesthetic property owing to tooth like color. Zirconia stabilized with Y_2O_3 has the best properties for these applications. The present work aims to study the effect of (5 and 10)Wt.% hydroxyapatite (HA) as additives to 3 mol% yttria stabilized zirconia (3YSZ) nano powder matrix. The green body samples were shaped by powder technology using cold pressing then sintering at (1300 and 1400)^{o}C. The 3YSZ/ HA nanocomposites samples were characterized by XRD to investigate phase stability with varying percent's of HA and different sintering temperatures, the mechanical properties (maximum bending strength and hardness) were investigated as a function of the HA content, the changes of the thermal expansion coefficient for composite samples were investigated using Dilatometer. The experimental results proved that additions of (5 and 10)Wt.% HA to 3YSZ matrix reduce both hardness and max. bending strength, while increasing sintering temperature from 1300^{o}C to 1400^{o}C leading to an increase in the hardness and bending strength for all composite samples. The results of thermal expansion test showed a reduction in the thermal expansion coefficient with presence of HA%, however the coefficient of 3YSZ/ 10%HA is closer to 3YSZ from 3YSZ/ 5%HA. EDS analysis shows improvement in the bioactivity of inert 3YSZ with HA% additions represented by increasing Ca and P ions on the composite samples after immersing in SBF for 6 days.

Keywords: *Zirconia, Hydroxyapatite, nanocomposites, bioceramic, dentalbioceramics, orthopedic bioceramic.*

1. Introduction

Zirconia-based ceramics have exceptional mechanical properties including (fracture toughness, strength and hardness), outstanding biocompatibility, aesthetics and heat conductivities that introduced it in dental and orthopedic applications over the last decades[1], however zirconia was classified as bioinert, which hampers their implantation in direct contact with bone. Furthermore, infections remain one of the leading causes of implant failure. There are three different pattern phases for Zirconia crystals: monoclinic (m), tetragonal (t) and cubic (c). Phase transformations of ZrO_2 associated with variation in crystal volume which produce internal stresses resulting early fracture during clinical applications [1]. When zirconia of monoclinic phase is heated, a transformation process to the tetragonal phase takes place at 1187 °C, and finishes at 1206 °C. During cooling stage, opposite transformation from the tetragonal to the monoclinic phase go on at 1052 °C and finishes at 1020 °C, it's called martensitic transformation. The volume of monoclinic unit cell is 4% more than the volume of tetragonal unit cell, this leads to the creation of ceramic flaws if no stabilizing oxides were used [2], many researches focused on using 3YSZ for prosthodontic applications (e.g., crowns, implants)and orthopedic implants, because this material exhibit the best combination of strength, toughness and hardness [3, 4]. In dental tissue replacement, high-strength 3YSZ has been used for many purposes, as root canal posts, crowns for other ceramics, fixed and removable dental prostheses, implant supports, and dental fillers [5].

The strategy of improving biocompatibility of various strong materials involves the incorporation of bioactive materials like hydroxyapatite. Hydroxyapatite (HA) is biocompatible and osteoconductive, having chemical composition and structure similar to mineral phase of bone and tooth tissues, it shows chemical reactions resulting a direct bond with hard tissue and promotes the new formation of bone tissues. However the disadvantage of HA is the poor mechanical strength (brittleness and low fracture toughness) that leads to limited fitness in load-bearing applications [6,7].In most applications of biomedical materials the mechanical properties are especially important, as well as the chemical reactivity of their surfaces for this reasons using bioactive ceramic such as HA has attracted a great attention for enhancing the biocompatibility of many strong biomaterials through the use of composite or as coating layer to achieve osseo integration and accelerate new bone formation beside high strength which is required for load-bearing applications such as dental/orthopedic implants [8]. Therefore, 3YSZ and other strong ceramics are considered a suitable matrix material for the HA-addition to produce biocompatible and strong composites to be used in load-bearing parts [9], while other researchers used HA as coating layer on porous zirconia substrate for bone tissue engineering scaffold, to facilitate bone generation around zirconia scaffold [10].

The present study concentrated on studying the properties of 3 mol% yttria stabilized zirconia (3YSZ) nano-powder through the addition of bioactive HA. The flexure strength, hardness, thermal expansion coefficient and XRD analysis were examined for the composites (3YSZ/ HA) samples as a function of the HA wt.% content using (1300, 1400) ^{o} C as different sintering temperatures.

2. Materials and Methods

2.1 Production of Materials

Commercially available 3YSZ nano powder (3YSZ, HWNANO, China) with particle size (< 100 nm) and high purity (99.99%).Prepared hydroxyapatite (HA) powder was used to produce composite samples. HA powder was prepared using simulated body fluid (SBF) solution and the raw materials are: Calcium nitrate tetra hydrate Ca $(NO_3)_2{\cdot}4H_2O$ (99**%**), Diammonium hydrogen phosphate $(NH_4)2HPO_4$ (99%) and NH_4OH solution. The procedure of this method includes disbanding of $(NH_4)_2HPO_4$ and $Ca(NO_3)_2{\cdot}4H_2O$ in discrete beakers in SBF solution for experimenting precipitation as shown in Figure 1.When all reagents dissolved in SBF, direct fine precipitation created small turbidity in the solution, filtering this solution using filter paper with addition of distilled water after that the remainder was saved for a day in oven. Dried material was milled in a mortar to fine particles [11].To produce composite samples varying amounts of HA (5 and 10) wt% were blended in 3YSZ powder. The mixed powder was ball-ground 3 h using a (SFM-1, QM-3SP2) planetary ball mill with rounds at 300 rpm in acetone as a dispersive media , then cold pressedby uniaxial pressure device (CT340-CT440) using cylindrical dies of (13× 26)mm andrectangular dies of(50×8×5) mm. All compacted samples were oven dried using electricblast dry box (WG43) at 100 ◦C for 24 hours. Firing process took place at two different temperatures (1300 and 1400) ◦C for 2 h with a heating rate of 5 ◦C/min.

3. Investigational procedures

The documentation and the crystallite phases of the composite samples after firing were categorized by x-raydiffractometer (Shimadzo, 6000) using Cukα radiation (λ = 1.5405 Å), and 40 KV/30 mA power applied.

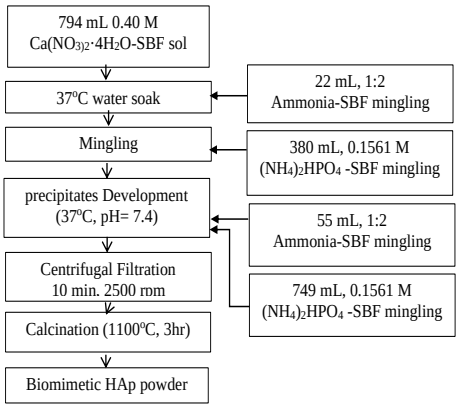

Fig. 1: Hydroxyapatite(HA) synthesis process

Analysis of particle size was extended using laser particle size analyzer (Bettersize2000). Thermal expansion curves were carried out to the sintered rectangular samples,the measurement of temperature range was100-600 °C via differential dilatometer in helium atmosphere.Microhardnesshad been measured in accordance with ASTM C 1327-99 with indentation load of 9.8 N with a dwelling time of 15 second.Vickers hardness was deliberated by the following equation.

$$Hv=1.\ 854(p/d2) \quad (1)$$

Hv, the Vickers hardness (Mpa), p, load (N), D, diagonal length of the indentation impression (μm)[12].

Three point bending was made according to ASTMC1161 procedure using computerized universal testing appliance with a speed test of 0.5 mm/min. The bending strength was calculated using the following equation.

$$(\sigma b)=3\ pfL/2wt2 \quad (2)$$

Where σb, is the bending strength (Mpa), pf, fracture load (N), w, width sample (mm), t, thickness sample (mm)[13] .Coefficient of thermal expansion (CTE) is important property in the field of esthetic restoration, where Zirconia used as a core covering by veneering ceramic, high difference in CTE between the cores and covering layer leads to a decrease in bond strength and produces clinical problems by chipping of veneering porcelain [14, 15].The coefficient of thermal expansion (CTE), α, for composite samples was measured by (Quickline – 05) dilatometer affording the appearance below:$\alpha = 1/L\circ\ .\ \Delta L/\Delta T$….(3)
Where, L◦: the length of sample at temperature of theambient, ΔL: the increasing in length and ΔT: is the temperature difference. The bioactivity test was investigated by submerging the samples in the simulated body fluid (SBF) which was prepared according to Kokubo protocol, 1990 [16], the test took place at 37 ºC for six days. EDS analysis was carried out for samples surfaces at the end of immersion time to check the
Concentration of (Ca and P) ions and giving an indicator to HA formation .The change in solution pH was checked every day by pH meter mention to the variation of (Ca and P) ions concentration in the solution during immersion time.

4. Results and discussion

4.1 Phase Evaluation

XRD patternof raw HA powder scanning of 5◦/min from 5◦ to 50◦ of 2Θ, in the peak locations agrees to the HA phase when matching its peaks with ASTM card No. (09-0432), as shown in Figure 2.The prepared HA powder was calcined at 1100°C for 3 hours. The powder displays HA peaks similar in the circumstance of prepared HA as shown in Figure 3, Figure 4 and Figure 5 resume the XRD patterns for all sintered powders, Yttria stabilized Zirconia(3YSZ) and yttria stabilized Zirconia(3YSZ)with different weight percentages of hydroxyapatite (HA) (5 and 10) wt% , scanned in diffraction angle (2Θ) from 10◦ to 60◦ upon heat treatment at 1300°C and 1400°C . The figures indicate that 3YSZ appears as major phase and all peaks are related to it as compared with XRD standard card no. (48-0224). and HA as unique phases in the biocomposites. In all cases HA peaks were well recognized and increased with increasing weight percent without decomposition to TCP or reacting withYsZ during both sintering (1300 and 1400)◦C, this result will serve in load-bearing applications because TCP is considered asbioresorbable material and dissolves faster than HA in body fluid .

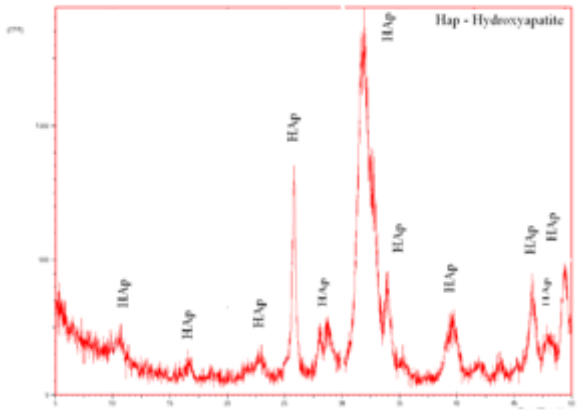

Fig. 2: XRD configuration of raw HA

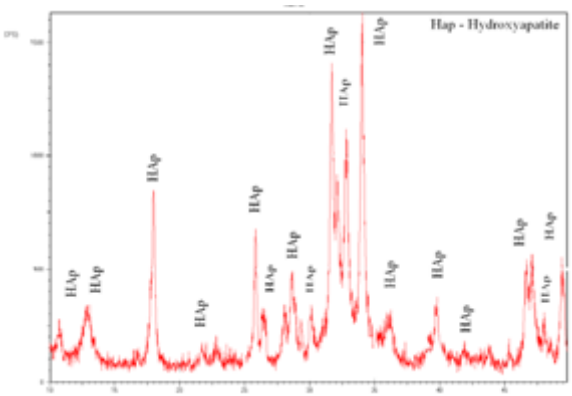

Fig. 3: XRD configuration of HA powder calcined at 1100oC.

4.2 Particle Size Measurement

Particle size of prepared HA was measured to provide about 4 µm as normal particle size as exposed in Figure 6.

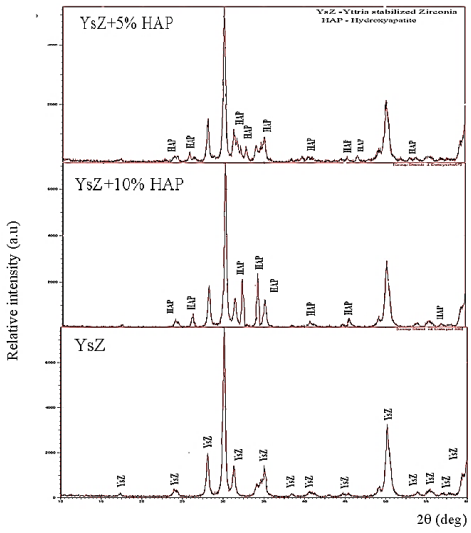

Fig. 4: XRD pattern of the3YSZ ,(3YSZ +10% HA) ,and (3YSZ +5% HA) sintered at 1300 °C.

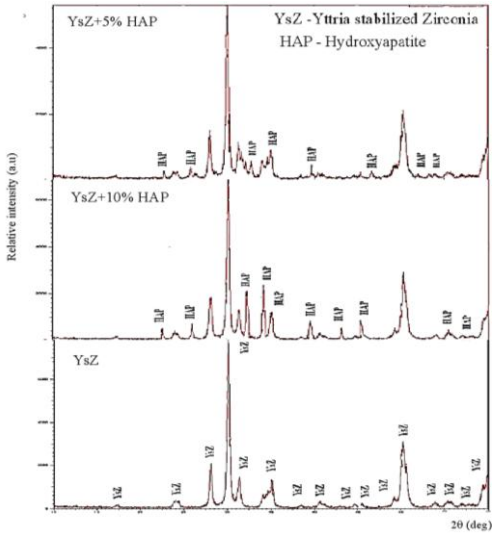

Fig. 5: XRD pattern of the 3YSZ ,(3YSZ +10% HA) ,and (3YSZ +5% HA) sintered at 1400 °C.

4.3 Mechanical Properties

The Max. bending strength and hardness were evaluated for the prepared samples as shown in Figure 7 and Figure 8 respectively.

Bending strength for pure 3YSZ in both sintering temperatureshave been reported within the range of 900–1200 MPa [14], these values were decreased with increasing HA% content. This may attributed to non-homogenous distribution and dispersion of large grains of HA in the 3YSZ matrix resulting to weak regains of brittle HA, another reason may be the difference in thermal expansion coefficient between HA and 3YSZ matrixthat will produce stressed structure. The same above figures illustrate that using different sintering temperature 1300 & 1400 °C resulting a change in the mechanical properties for both pure and composite 3YSZ. The strength of the pure 3YSZ was increased from 1087MPa at 1300°C to 1101MPa at 1400°C sintering temperature. The same behavior was shown for composite samples with (5& 10) Wt.% HA, the bending strength rises with increasing sintering temperature; the same scenario was repeated with hardness values were increasing HA% reduces hardness of 3YSZ, while increasing sintering temperature rising hardness . It is known that sintering procedure has an effect on the mechanical strength and microstructure of ceramic materials. This result was confirmed by Kong Y. et.al. 2005 [9], who added HA to ZrO_2–Al_2O_3nano-composite and got a reduction in mechanical properties. Figure 9 shows an increasing in shrinkage volume rate with increment of HA%, this comes in agreement with other research used bioglass as additive to 3YSZ [17] that may attributed to use different scale of particle size for HA and nano 3YSZ. At the same time it is clear that the higher sintering temperature 1400°C led tohigher volume shrinkage for pure and composite samples resulting from densification and a reduction in porosity leading to higher bending strength and hardness for all samples [18]. Figure10 shows that at the same sintering temperature HA additions led to slightly decrease in the thermal expansion coefficient of the composites compering with pure 3YSZ. Figure11 displays that the reduction in thermal expansion coefficient for composite samplestook place at both sintering temperature (1300& 1400) °C.It is well known that thermal expansion coefficient of 3YSZ is 11-12 × 10^{-6} $°C^{-1}$ [19], after HA additions the difference in thermal expansion coefficient didn't exceed (0.1-0.5) × 10-6 $°C^{-1}$ for all temperatures, these differences may promote the generation of stress fields around the grains of 3YSZ [17], wl 2θ(deg) another reason for reduction in bending strengtl..

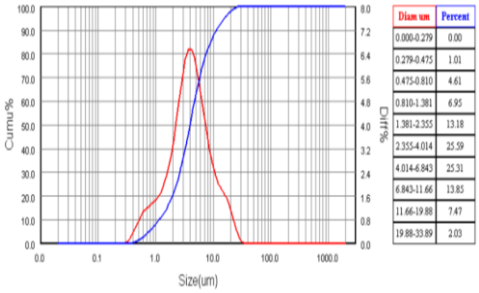

Fig. 6: Particle size analysis of the prepared HA powder.

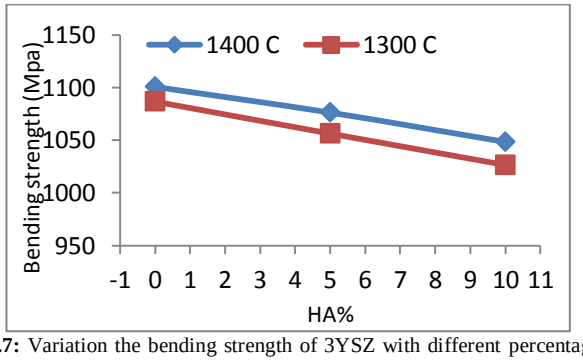

Fig.7: Variation the bending strength of 3YSZ with different percentages of HA

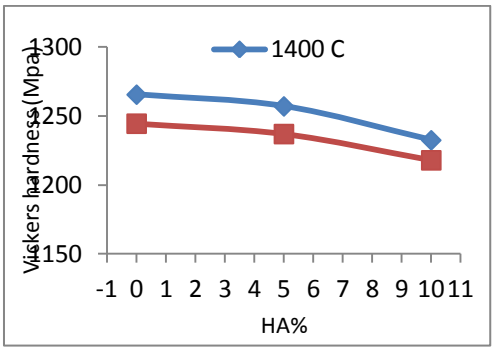

Fig. 8: Variation Vickers hardness of 3YSZ with different percentages of HA

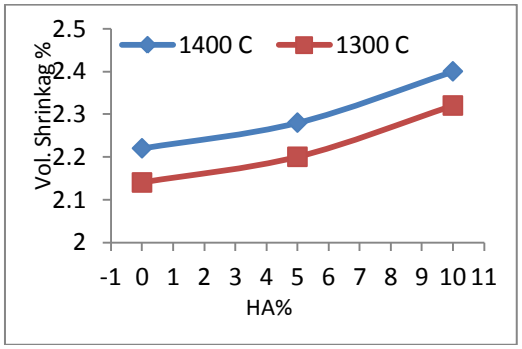

Fig. 9: Variation the shrinkage rate of 3YSZ with different percentages of HA

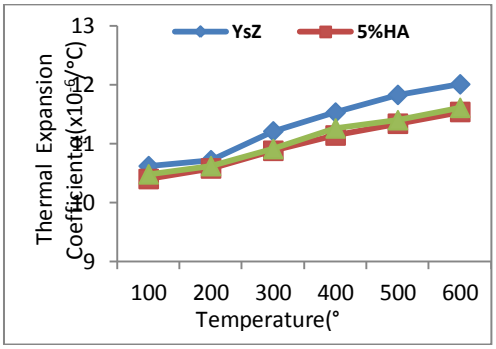

Fig. 10: Variation the thermal expansion coefficient of 3YSZ with different percentages of HA sintered at 1300°C.

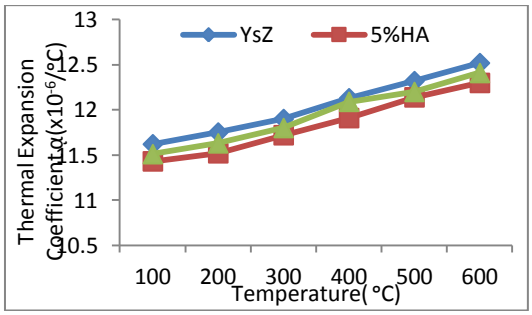

Fig. 11: Variation the thermal expansion coefficient of 3YSZ with different HA% sintered at 1400°C.

Figure 12 and Figure 13 illustrate that variation of pH in SBF started at the second immersion day for composite samples giving good indicator to HA role as active biomaterial in contrast with 3YSZ sample, were the pH stayed constant in all immersion days. We can observe that pH variation for composite samples sintered at 1300°C is more than samples sintered at 1400°C, that may attributed to high densification at 1400 °C leading to high shrinkage and low porosity, all above produce samples with lower surface area leading to a reduction in reaction rate and pH variation. EDS results in figure 14 and figure 15illustrate that increasing HA% in the composite samples led to an increase in the concentration of Ca and P ions on the sample surfaces when they immersed in SBF for 7 days, giving an indicator for HA precipitation and increasing bioactivity and ability to form bonding layer with host tissue. These results were confirmed by Kong Y. et.al. 2005 [9] who found that using HA as additive to 3YSZ matrix lead to improve the bioactivity and biocompatibility to the inert ceramic.

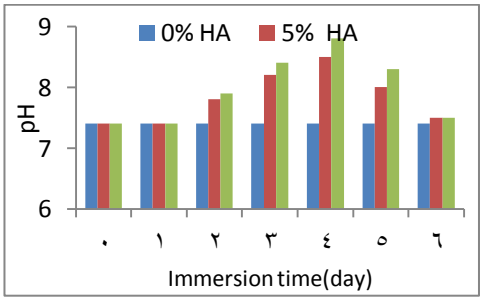

Fig. 12: Variation the pH of SBF for of 3YSZ with different percentages of HA sintered at 1300°C.

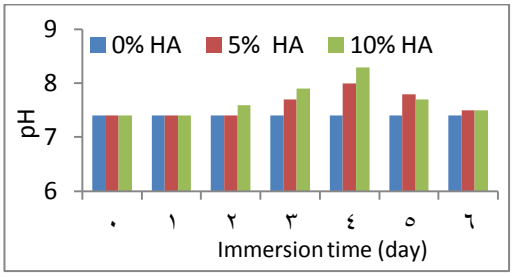

Fig. 13: Variation the pH of SBF for of 3YSZ with different percentages of HA sintered at 1400°C.

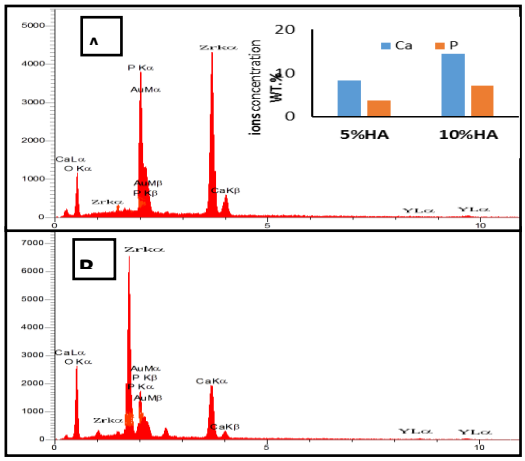

Fig. 14: EDS analysis for immersion surfaces of 3YSZ with A) 5% of HA, B) 10% of HA sintered at 1300°C.

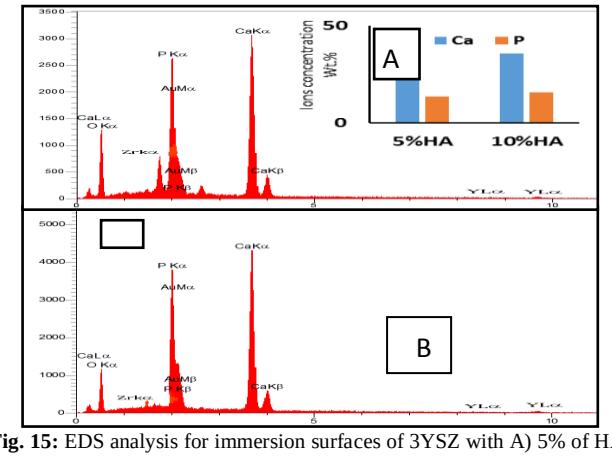

Fig. 15: EDS analysis for immersion surfaces of 3YSZ with A) 5% of HA, B) 10% of HA sintered at 1400°C.

5. Conclusions

The outcomes of this work demonstrates that the addition of (5,10)% HA to 3YSZ matrix led to a reduction in the bending strength and vickers hardness. However, they are still more than that for cortical bone, also there is a slight decrease in thermal expansion coefficient for composite samples of 3YSZ / HA compering with pure 3YSZ. In vitro, EDS result showed the ability of 3YSZ/ HA samples to form Ca-P-rich layer on the surface after immersing in SBF suggesting that the addition of HA led to form bonding layer with host tissue the property that is not found in pure 3YSZ. These results indicate that HA prepared by method used in this work may improve the bioactivity of new zirconia based composites. The next step of investigation should be the phase analysis of composites and description of the microstructure.

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