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Synthesis and characterization of polymer additives based nanocrystalline zirconia by sol gel method for teeth coatings

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ABSTRACT

In order to obtain a bioactive material; with high mechanical strength, high fracture toughness and aesthetic properties needs to be fabricated. Such properties can be obtained in ceramics. Zirconia ceramics have gained favor as restorative materials because of their excellent mechanical properties; they have high strength and toughness, good biocompatibility, and relatively good aesthetic properties. But the problem with zirconia is inertness with the body fluid and it resists the formation of bonds with bones and tissues. This problem can be minimized by some biocompatible additives. This explorative study was performed to examine a possible impact of polymer on ZrO_2 nanoparticles (NPs). Along with effect of reaction temperature (50, 100 and 150°C) has been investigated on structural and mechanical properties of polymer additive zirconia. XRD results illustrate the partially stabilized zirconia (PSZ) however, monoclinic content decreases with increase in reaction temperature. A decrease in crystallite size has observed due to structural changes. A decrease in particle size has found at higher reaction temperatures. The mechanical properties of the samples were characterized by Micro Vickers Hardness tester and hardness of the samples is in the range of 590HV to 1000HV.

1. INTRODUCTION

Among metal oxides, zirconium oxide (zirconia) represents one of the most studied oxide material because of its various applications (Rathod et al. 2010). It has important physical and chemical properties e.g. high value of hardness, higher melting point (~2600°C), high corrosion resistance and biocompatibility (Balakrishnan et al. 2013). Although it has been widely studied over few decades, the interest of the researchers is still increasing due to the wide range of its applications. Among these applications most important ones are bioceramics, gas sensors, catalysts and photonics (Heiroth et al. 2010).

Last few decades nano-crystalline materials, specifically zirconia (ZrO_2) nanoparticles (NPs), have gained a lot of potential since they exhibit unique physical and chemical properties (Zawawi et al. 2013). ZrO_2 NPs have properties which are significantly different from their counterparts (Choi et al. 2005).

At ambient conditions, pure zirconia exists in three solid polymorphs: Monoclinic phase (m-phase), that is, thermodynamically stable at temperatures below1172°C, tetragonal phase (t-phase), stable at the temperature range of1172–2347°C, and cubic structure (c-phase), stable above 2347°C (Prasad et al. 2011). Among all phases tetragonal zirconia (t-ZrO_2) has high mechanical strength, fracture toughness and a

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Young's modulus similar to that of stainless steel alloy (Piconi and Maccauro 1999). It is used as a dental structural material for multiple unit posterior bridges (Mahmood et al. 2013). But tetragonal zirconia is metastable (Davar et al. 2013). Stabilized t-phase can be achieved by addition of some polymers (Shukla et al. 2003). However reaction temperature and initial synthetic conditions has pronounced effect on the transformation of low temperature phase (monoclinic) to high temperature phase (tetragonal) of zirconia (Li et al. 2013). The martensitic transformation from monoclinic to tetragonal phase could lead to 3-5% volume decrease and consequently increase in density (Denry and Kelly 2008) which is one of the requirements for the implants in biomedical applications. Hence, such transformation is favorable for the development of zirconia bioceramics (Duan et al. 2013).

Polymers additive zirconia NPs have been synthesized using different experimental techniques such as co precipitation (Maheswari et al. 2013), ball milling (Adam et al. 2008) and sol gel (Majedi et al. 2014) etc.

In this research article we have synthesized polymer additive ZrO_2 nanoparticles at different reaction temperatures and their structural and mechanical properties are investigated.

2. EXPERIMENTAL DETAILS

$ZrOCl_2.8H_2O$ (Sigma–Aldrich, 99.99% pure), and NH_3 anhydrous (Sigma–Aldrich, 99.99% pure) were used without further purification. Water was deionized (DI) prior to use.

2.1 Synthesis of Nanoparticles

Zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$) was used as a precursor of zirconia, which was mixed in DI water to form 0.1M solution of pH 2. NH_3 was added into 0.1 M solution of zirconium oxychloride to form a milky sol. NH_3 was also added to vary the pH of sol from acidic (pH 2) to basic (pH 9). Sol results in formation of $Zr(OH)_4$ and NH_4Cl along with release of 7 water. Meanwhile, polymers were added in synthesized zirconia sols. Shiny and transparent sol was obtained after stirring at room temperature for five hours. Zirconia sol was heated at different reaction temperatures (50, 100 and 150°C) for formation of powders.

2.2 Characterizations

A wide angle X-ray diffractometer (Bruker D8 Advance) was used to study the crystalline structure of the NPs. The Cu K-alpha radiation source was used. K-beta filter was used to eliminate interference peak. For morphological study scanning electron microscopy (Hitachi S-3400N) was used. Mechanical properties were studied by using Shimadzu Micro Vickers hardness indenter.

3. RESULTS AND DISCUSSION

In different reports polymers have been used as organic additive in zirconia (Suciu et al. 2008, Suciu et al. 2006 and Suciu et al. 2003). However, in polymer additive zirconia pH plays an important role. Strongly acidic medium results in oxidize the polymers. Therefore, pH of polymer additive zirconia was set to 9, so polymers do not oxidized rapidly (Suciu et al. 2008). The detailed study of polymer additives shows that they act as a capping agent which consequently leads to the transformation of phase from monoclinic to tetragonal (Heshmatpour et al. 2011).

XRD patterns of as-synthesized polymer additive zirconia (PZ) show polycrystalline nature at all reaction temperatures as depicted in Fig. 1. At reaction temperatures 50°C to 150°C peaks at approximately 23. 2º, 31.9º and 41.2º correspond to the (011), (111) and (021) planes of monoclinic zirconia (m-ZrO_2) [JCPDS 13-307]. However, peaks correspond to 47.9°, 53.5º, 59.0º, 68.8º, 73.5° and 78.1º correspond to the (221), (113) (123) (004) and (330) planes of tetragonal zirconia (t-ZrO_2) [JCPDS 17-923], respectively. Presence of t-ZrO_2 at lower temperatures can be evidence by presence of (004) peak (Srinivasan et al. 1991). High temperature t-ZrO_2 is present even at low reaction temperature due to the incorporation of polymers. Polymers addition results in partially stabilized zirconia (PSZ). Heshmatpour et al. obtained same results at 400°C using two organic additives (Heshmatpour et al. 2011) but here we achieved same results at very low reaction temperature (~50°C). Moreover, according to literature (Tsalouchou et al. 2008) PSZ usually obtained by addition of metal oxide as stabilizer but in present study PSZ has obtained in the absence of stabilizer.

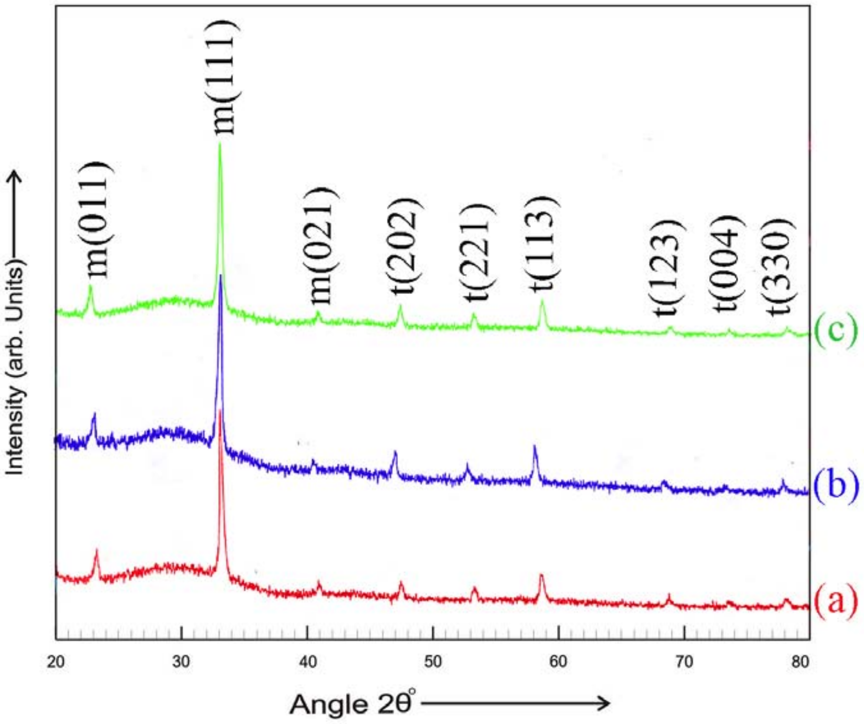

Fig. 1 XRD patterns of PZ at reaction temperature a) 50, b) 100 and c) 150°C

Volume fraction of monoclinic phase (V_m) was calculated by the following equations, as given in Eqs. 1-2 (Sahu and Rao 2000);

$$X_m = \frac{I_m(111) + I_m(011)}{I_t(113) + I_m(111) + I_m(011)} \tag{1}$$

$$V_m = \frac{(1.311X_m)}{1 + (0.311X_m)} \tag{2}$$

Where, I_m and I_t denote to the intensities of monoclinic and tetragonal peaks respectively. Whereas, volume fraction of tetragonal phase was calculated by using Eq. 3;

$$V_t = 1 - V_m \tag{3}$$

Volume fraction of monoclinic phase decreases with the reaction temperature. The volume fraction ratio of monoclinic and tetragonal PZ powders is calculated by Eq. 2. The results are summarized in Table 1. The fraction of t-phase retained at room temperature may be due to crystallite size effect (Mahmood et al. 2013). Fig. 2 shows the variation in tetragonal content with reaction temperature.

Table 1. Variation in tetragonal to monoclinic ratio (t:m) with reaction temperature

Reaction Temperature (°C)	t:m
50	27:73
100	31:69
150	35:65

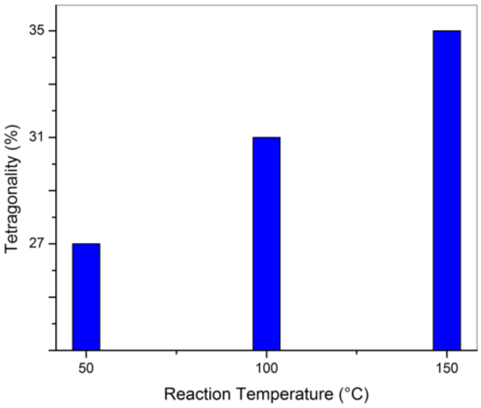

Fig. 2 Variation in tetragonal content with reaction temperature

Crystallite size was calculated by using Debye Scherer's formula is given in Eq. 4 (Cullity 1956).

$$D = \frac{0.9\lambda}{\beta Cos\theta} \tag{4}$$

Where D is grain size of the PZ powders, β is the width at half maximum (FWHM) of a Bragg peak, λ is the X-ray wavelength (1.5406Å) and θ is the Bragg angle. Crystallite size was calculated at reaction temperature 50°C is 25.04nm. With increase in reaction temperature, crystallite size of PZ NPs decreases up to 22.23nm [Fig. 3]. **Decrease in crystallite size is due to some structural changes occurs with reaction temperature.**

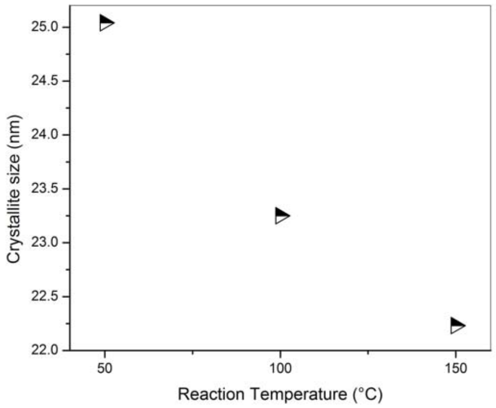

Fig. 3 Crystallite size of PZ NPs at different reaction temperatures

Dislocation lines/m^2 (dislocation density) was calculated by 1/D^2, where D is the crystallite size (m). Relatively lower dislocation lines/m^2 was calculated for polymer additives zirconia NPs at different reaction temperatures is shown in Fig. 4. Lower dislocation density produces strong bonding between atoms. Strong bonding is preferable for biological implants and to cure diseases (Bashir et al. 2014a).

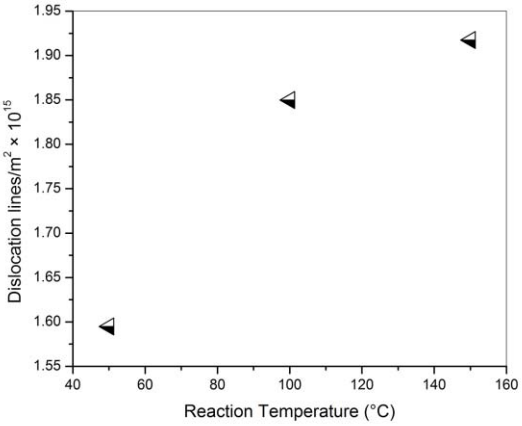

Fig. 4 Dislocation lines/m^2 (Dislocation density) of PZ NPs at different reaction temperatures

Monoclinic and tetragonal zirconia phases are differed by unit cell volume and density. Unit cell volume and density of m-ZrO_2 and t-ZrO_2 is calculated by using Eqs. 5 - 7.

$$V_{Monoclinic} = abcSin\beta \tag{5}$$

$$V_{Tetragonal} = a^2 b \tag{6}$$

$$\rho = \frac{1.66042 \sum A}{V} \tag{7}$$

Where a, b, and c are lattice parameters and ΣA is sum of atomic weights of all the atoms present in unit cell (Cullity 1956).

Change in zirconia crystal structure depends upon the volume of the unit cell, actually this OH ions from water are responsible for monoclinic content as well as results slight larger volume. Whereas, shrinkage in volume leads to transformation of monoclinic phase to tetragonal. Volume of samples decreases with increase in reaction temperature is due to removal of OH ions. OH ions produce tensile stresses material which results in larger volume and removal of OH ions lead to shrinkage in volume as depicted in Fig. 5.

Density is inversely proportional to unit cell volume [Eq. 7]. Density of PZ NPs increases with reaction temperature, as the unit cell decreases with release of OH ions. Moreover, high x-ray density of PZ NPs (~ 5.7g/cm^3) strengthens the material; which is one of the requirements for bone implantations and grafting (Bashir et al. 2014b). Fig. 6 depicts the density vs. reaction temperature graph.

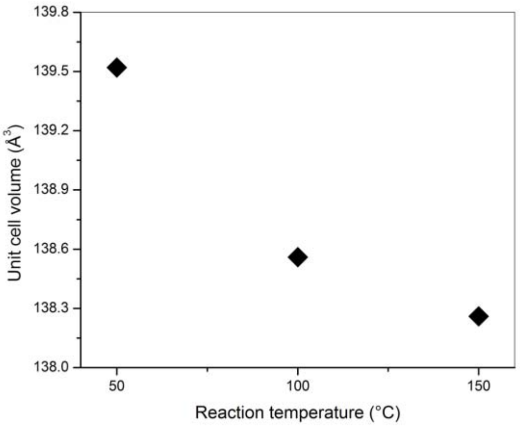

Fig. 5 Unit cell volume of PZ NPs as a function of reaction temperatures

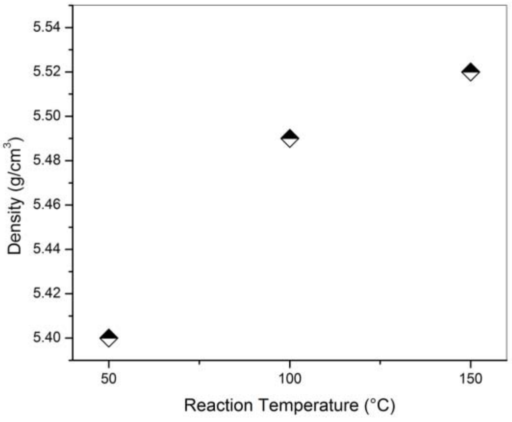

Fig. 6 Density of PZ NPs as a function of reaction temperatures

For implants and grafting applications mechanical properties along with structural properties are important. Mechanical properties of ZrO_2 are pertained to its fine grained and microstructure. Mechanical properties are degraded usually in the presence of mix (monoclinic and tetragonal) phases. This behavior is well known if water molecules are present (Piconi and Maccauro 1999). The presence of water molecules causes reduction in strength, toughness and density, and an increase in monoclinic phase content. For hardness measurements indentation tests was performed using the Micro Vickers test. The dwell time at 4.9N load was equal to 15 s in agreement with the time recommended by the standard for Vickers hardness testing (ASTM-C1327). Hardness of the samples increases with increase in reaction temperature due to removal of OH ions. Hardness of the samples is in consistent with XRD data where monoclinic phase content decreases and density of the samples increase with reaction temperature.

Table 2: Hardness of samples with Reaction temperature

Reaction Temperature (°C)	Hardness (HV)
50	840
100	867
150	956

4. CONCLUSIONS

In this research paper NPs of polymer additive zirconia (PZ) were synthesized at different reaction temperatures (50, 100 and 150°C) through sol-gel method. Zirconium oxychloride octahydrate ($ZrOCl_2$. $8H_2O$) was used as a precursor of zirconia and NH_3 was used as gelation agent. Polymer was added into ZrO_2 sol as capping agent. XRD results demonstrated the presence of high temperature tetragonal phase at low temperature (50°C) due to presence of polymers. Crystallite size of PZ NPs was found to decrease with increase in reaction temperature. Reaction temperature has significant effect on unit cell volume and density of zirconia. Shrinkage in unit cell volume and increase in X-ray density was observed with reaction temperature. Hardness of the samples also increased with reaction temperature due to removal of OH ions, decrease in monoclinic content and increase in density of samples.

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