Chapter 4

Thermal Treatment of ZrO₂ Nanoparticles

4.1 Introduction

Recently the properties of zirconia nanoparticles are extensively studied owing to its unique phase dependent physical and chemical properties useful for various applications. Zirconia nanoparticles possess high oxygen ion conduction and refractive index and hence used as catalysts [190–194] and oxygen sensors [195]. Further, their high strength, toughness, hardness, wear and thermal shock resistance properties led to the fabrication of zirconia based components in applications such as automobile engine, wire drawing dies and cutting tools. Also zirconia based coating is used to improve the tribological properties of materials surfaces.

The martensitic phase transformation of \( t \rightarrow m \) is important for its mechanical properties. This phase transformation results in volume expansion
which thereby improves the fracture toughness of coatings made of metastable tetragonal zirconia nanoparticles. Various synthesis techniques such as sol-gel process [148], chemical precipitation method [196], forced hydrolysis [197], hydrothermal method [198, 199], thermal plasma [194], microwave irradiation [200], and two phase process [201] have been used to stabilize tetragonal zirconia at room temperature. Among them, surfactant assisted chemical precipitation method is cost effective and feasible to control the phases by optimizing the process parameters like precursor, solvent, surfactant, mineralizer, calcination temperature and dopant concentration. Through suitable choice of parameters the grain size can be controlled within critical size which results in excess oxygen vacancies required for tetragonal phase stabilization at room temperature. This can be achieved by the slow polymerization of surfactant capped zirconia tetramers [56, 146]. The surfactant stabilizes the tetramers against agglomeration and thereby regulates the grain size of zirconia nanoparticles. The efficiency of regulation depends on the nature of surfactant and is large for highly stabilized zirconia tetramers. Further the calcination temperature used for conversion of zirconium hydroxide to zirconia nanoparticles determines their phase. Reports show that at higher calcination temperature grains coalesce each other and consequently the size of resulting nanoparticles will be larger than the critical value. This lowers the surface energy for monoclinic zirconia formation and hence happens to be the predominant one. However the coalescence can be regulated at certain calcination temperatures by grafting surfactant (having higher decomposition temperature) on the surface of zirconia tetramers. Though studies related to influence of annealing temperature on phase transformation have been reported, effect of both surfactant and an-
nealing temperature on controlling zirconia phases is scarcely reported. In this context, the present chapter is intended to investigate the phase transformation of surfactant capped hydrous amorphous zirconia $\text{Zr(OH)}_{4x}\text{H}_2\text{O}$ (HAZ) calcined at 500, 600, 700 and 800 °C.

4.2 Experimental Methods

4.2.1 Synthesis of zirconia nanoparticles

Initially surfactant (PVP / CTAB) capped zirconium hydroxide is synthesized by polymerization of surfactant stabilized zirconia tetramers with hydroxyl ions released from alkaline mineralizer $\text{NH}_4\text{OH}$. The procedure for the synthesis is explained in Chapter 3. To analyze the influence of surfactant on phase transformation, the as-synthesized polymeric / anionic surfactant capped zirconium hydroxide is calcined at 500, 600, 700 and 800 °C for getting zirconia nanoparticles.

4.2.2 Characterization techniques

The samples are characterized using X-ray diffraction (XRD), Thermo-gravimetry (TG), Fourier transform infrared spectroscopy (FTIR), micro-Raman and Photoluminescence (PL) spectroscopy techniques. The specifications of X-ray diffractometer, photoluminescence and micro-Raman spectrometer are given in chapter 3. Thermal degradation of samples (16.45 mg and 14.044 mg of CTAB and PVP capped zirconium hydroxide respectively) is carried out in SDT Q600 V20.9 Build 20 TGDTA instrument in nitrogen
atmosphere (flow rate: 100 ml/min) in the temperature range of 25 - 900 °C. The Fourier transform infrared spectra (FTIR) of zirconia nanoparticles were recorded at room temperature on a Thermo Nicolet, iS10 FT-IR spectrometer with wavenumber ranging from 400 to 4000 cm$^{-1}$. The sample for FTIR measurement is prepared by pelletizing the calcined zirconia nanoparticles with KBr.

4.3 Results

4.3.1 X-ray diffraction analysis

The structural analysis of samples calcined at different temperatures is carried out by comparing the 2θ values of diffraction peaks with JCPDS card numbers 37-1484, 65-2357 (monoclinic - M) and 14-0534, 17-0923, 42-1164 (tetragonal - T). Fig. 4.1 shows the diffractograms of samples calcined at 500, 600, 700 and 800 °C with tetragonal (T) and monoclinic phases (M). The nanoparticles synthesized using PVP calcined at 500 - 700 °C shows prominent peaks (Fig. 4.1a) corresponding to tetragonal zirconia as compared to CTAB assisted samples (Fig. 4.1b). The percentage of monoclinic content with respect to tetragonal in the as-calcined PVP and CTAB samples is estimated using the equation [202]:

$$f_m = \frac{I_m(\overline{1}11) + I_m(111)}{I_t(111) + I_m(\overline{1}11) + I_m(111)} \times 100,$$

(4.1)

where $I_m(\overline{1}11)$ and $I_m(111)$ are the area under monoclinic peaks ($\overline{1}11$) and (111), and $I_t(111)$ corresponds to area of tetragonal peaks obtained using Gaus-
sian curve fitting. The percentage of monoclinic content for the PVP and CTAB samples calcined at 500, 600, 700 and 800 °C respectively are ~7, ~38, ~45, ~64 and ~30, ~53, ~57, ~58. It is observed that at higher temperatures (>500 °C), the percentage of tetragonal to monoclinic transformation in CTAB samples is less than PVP due to higher probability of crystallization of randomly oriented polymeric sheets of HAZ to monoclinic zirconia [203].

![XRD spectra](image)

Figure 4.1: XRD of PVP and CTAB capped zirconium hydroxide samples calcined at 500, 600, 700 and 800 °C

### 4.3.2 Thermogravimetric analysis

The surfactant gets chemisorbed on the metallic ions to stabilize them against agglomeration during hydrolysis and hence not removed completely during washing of metal hydroxides. However studies show that surfactant gets removed completely at specific calcination temperatures that are determined by
the nature of interaction between surfactant and metallic ions released from mineralizer [204, 205]. Stronger the interaction greater will be the decomposition temperature of surfactants and the structure of zirconia nanoparticles [146]. In order to understand the surfactant role in phase transformation mechanism at higher crystallization temperature, the as-synthesized PVP and CTAB capped HAZ are subjected to TG analysis (Fig. 4.2a and b). A significant difference in decomposition temperature of surfactants is observed between the samples. From the graph, the weight loss due to removal of surface water from surfactant capped HAZ in the temperature range 30 °C to 200 °C is 19.5 % (2.738 mg) for PVP and for CTAB it is 24.6 % (4.047 mg). Further, the thermal degradation of PVP takes place in the temperature range 488 - 555 °C with a weight loss of 0.5027 % (0.071 mg). But for CTAB it is in the temperature range 415 - 495 °C with a weight loss of 0.5864 % (0.096 mg). The volatile products formed during degradation of PVP and CTAB [206, 207] is investigated from FTIR spectra of HAZ sample thermal treated at different temperatures.
4.3.3 Fourier transform infrared spectroscopy analysis

The FTIR spectra of as-synthesized PVP capped zirconium hydroxide and their annealed samples are presented in Fig. 4.3a. The spectra of zirconium hydroxide exhibits vibrational bands at 432 and 668 cm$^{-1}$ attributed to Zr-O bond and those at 1257, 1338, 1627, 2832 and 2885 cm$^{-1}$ which indicates PVP capping of zirconium hydroxide. The vibrational bands observed at 1257 cm$^{-1}$ and 1338 cm$^{-1}$ is ascribed to C-H bending vibration of methylene groups and CH$_2$ bending vibrations in pyrrolidone ring of PVP respectively [208]. Moreover the broad band at 3430 cm$^{-1}$ corresponds to hydroxyl groups at defect sites. Large red shift of 1667 cm$^{-1}$ band to 1627 cm$^{-1}$ indicates strong adsorption of PVP molecules on surface of zirconium hydroxide through the oxygen atom of C=O. Further, the vibrational band at 2855 cm$^{-1}$ is due to stretching vibration of C-H bond in pyrrolidone ring of PVP and hence confirms adsorption of PVP.
molecules on the surface of zirconium hydroxide.

FTIR spectra of CTAB capped zirconium hydroxide and samples calcined at 500, 600, 700 and 800 °C are shown in Fig. 4.3b. Before calcination spectra shows vibrational bands at (i) ~ 438 cm\(^{-1}\) due to Zr-O bond vibration, (ii) ~ 1337 cm\(^{-1}\), ~ 1574 cm\(^{-1}\) and 1627 cm\(^{-1}\) attributed to CH\(_2\) scissoring mode of vibration and O-H bending mode of water around the bound head group, and (iii) at ~ 3427 cm\(^{-1}\) corresponds to O-H stretching frequency of water solvating the surfactant CTAB. This confirms the capping of CTAB on zirconium hydroxide which stabilizes the polymerized zirconia tetramers against agglomeration.

4.3.4 Micro-Raman spectroscopy analysis

Phase translation of surfactant capped hydrolyzed zirconia tetramers [Zr\(_4\)(OH)\(_{16}\)(H\(_2\)O)\(_8\)] with calcination temperature is also analyzed using micro-Raman spectra of the samples. The spectra (Fig. 4.4 and 4.5) show that tetragonal and monoclinic phases are present in both samples. PVP samples calcined at 500 °C show prominent Raman modes corresponding to tetragonal ZrO\(_2\) at 241 (B\(_{1g}\)), 269 (E\(_g\)), 315 (B\(_{1g}\)), 405, 465 (E\(_g\)), and 642 (B\(_{1g}\)) cm\(^{-1}\); and monoclinic zirconia peaks at 375, 473 and 577 cm\(^{-1}\). For samples calcined at 600 °C and above, the intensity of tetragonal modes decreases while for monoclinic modes the intensity increases. The ratio of tetragonal Raman peak height corresponding to 642 cm\(^{-1}\) to that of monoclinic peak at 473 cm\(^{-1}\) in PVP sample calcined at 500 °C is found to be ~ 2.2. But this greatly reduced to ~ 0.68, ~ 0.6 and ~ 0.46 in PVP samples calcined at 600, 700 and 800 °C respectively due to decomposition of PVP. The small difference with increase in calcination
temperature is attributed to increased monoclinic content which slow down the t → m transformation [192].

The CTAB samples calcined at 500 °C showed prominent Raman modes (Fig. 4.5) of tetragonal zirconia at 271, 314 and 638 cm⁻¹, and monoclinic modes at 240, 332, 340, 474 and 613 cm⁻¹. At 700 °C, the mode corresponding to tetragonal zirconia at ∼ 640 cm⁻¹ is disappeared; conversely ∼ 263 cm⁻¹ mode became prominent which indicates prevention of tetragonal to monoclinic phase transformation. The same trend is seen with CTAB sample at 800 °C as confirmed by tetragonal Raman mode at ∼ 638 and 650 cm⁻¹ on deconvolution of vibrational band in the region of 588 - 677 cm⁻¹. The ratio of peak heights of tetragonal and monoclinic modes at ∼ 638 cm⁻¹ and ∼ 474 cm⁻¹ respectively of CTAB samples at 500 °C is ∼ 0.68 which is one-third of PVP sample at same temperature. But at 800 °C the ratio remains same for both samples. This is attributed to higher percentage of randomly oriented hydrolyzed tetrameric units in HAZ which crystallizes to monoclinic content and consequently slows down the phase transformation of ordered units to monoclinic zirconia at thermal treatment greater than surfactant decomposition temperature [203]. Hence the tetragonal to monoclinic phase transformation is slower at 600, 700 and 800 °C in CTAB than the respective PVP samples.

### 4.3.5 Photoluminescence spectroscopy analysis

The presence of excess oxygen vacancies which stabilizes the tetragonal zirconia nanoparticles of critical size [209] is analyzed from PL spectra (Fig. 4.6). The oxygen vacancies act as F centres and electron trappers and hence greatly influence the luminescent property of zirconia nanoparticles [157]. The spec-
Figure 4.4: Micro-Raman spectra of PVP capped zirconium hydroxide calcined at 500, 600, 700 and 800 °C

Figure 4.5: Micro-Raman spectra of CTAB capped zirconium hydroxide calcined at 500, 600, 700 and 800 °C
tra of both samples showed four major peaks centered at ∼ 340, ∼ 405, ∼ 432, and ∼ 458 nm. The ∼ 340 nm peak confirms the presence of excess oxygen vacancies for tetragonal phase stabilization [158]. The peaks in the region 400 to 460 nm is due to radiative transition of electrons from F centre to holes in valence band [210, 211].

![PL spectra of PVP and CTAB zirconia samples excited at 300 nm](image)

**Figure 4.6**: PL spectra of PVP and CTAB zirconia samples excited at 300 nm

### 4.4 Discussion

Reports show that high temperature phases of zirconia namely tetragonal and cubic have potential applications typically at room temperature [212–217]. Consequently the mechanism to stabilize tetragonal and cubic phases in zirconia at room temperature and the associated phase transition has to be investigated in detail. The literature shows that high temperature phases can be stabilized in bulk zirconia through doping [218, 219]. However in nanocrystalline zirconia, the synthesis technique, process parameters like solvent, mineralizer, surfactant and crystallization temperature determines the zirconia phase for a given experimental condition. The mechanism of room temperature stabiliza-
tion of high temperature phases in zirconia depends on domain size which can be divided into three different regions: (i) micrometer-sized zirconia (> 1 µm) (ii) submicron size ranging from 100 nm - 1 µm and (iii) nanocrystalline zirconia of crystallite size less than 100 nm. In micrometer-sized zirconia, the tetragonal and cubic phase can be stabilized through (i) introducing oxygen vacancies at higher temperature [220] (ii) annealing in reduced oxygen partial pressure at relatively lower temperature [221] (iii) doping trivalent cations in zirconia structure [218]. The density of oxygen vacancies determines the degree of stability of high temperature phases. Consequently the decrease in density of oxygen ion vacancies leads to phase transformation from tetragonal to monoclinic [222]. However tetragonal phase can be stabilized in pure nanocrystalline zirconia at room temperature by reducing its average crystallite size below a critical value which is determined by surface energy, strain energy, internal and external hydrostatic pressure, structural similarities, foreign surface oxides, anionic impurities, water vapour and point defects. The surface energy theory predicts that for an isolated, strain free, nanocrystalline zirconia, the tetragonal phase can be stabilized if its crystallite size is less than 10 nm [145, 223]. At this critical size, the surface energy in these nanocrystals tends to have a minimum value to stabilize the tetragonal phase and the so formed nanocrystals have spherical or near-spherical surface morphology. However the phase transformation from tetragonal to monoclinic phase results in morphological change from spherical to a spindle or rod like shape [224]. Further, the calcination temperature determines the percentage of tetragonal phase in zirconia nanocrystals. At intermediate calcination temperature, tetragonal to monoclinic phase transformation takes place and at very high temperatures it
becomes monoclinic zirconia. The critical size for monoclinic to tetragonal phase transformation depends on the surface energy. The phase transformation temperature from monoclinic to tetragonal phase increases with increase in crystallite size above 10 nm. Consequently the bulk monoclinic zirconia transforms to tetragonal phase at 1175 °C [225].

The critical crystallite size for tetragonal phase stabilization determined by thermodynamic model is applicable only for strain free, single domain zirconia nanocrystallites. However for zirconia nanocrystallites of spherical or near-spherical shape, the surrounding atmosphere or excessive aggregation of nanocrystallites gives rise to interfacial energy which causes a change in surface energy values for the involved phases and thereby affect the critical size required for tetragonal phase stabilization. Thus the critical size for tetragonal phase stabilization in a strain free tetragonal particle in the aggregated state is calculated to be 33 nm [225, 226]. In addition to interfacial energy, the strain energy within the aggregated nanocrystallites leads to lattice defects which alter the energy balance for stabilization of tetragonal phase at room temperature and thereby the critical size. The surface energy theory predicted that tetragonal domain of critical size 33 nm within the aggregated nanocrystallites should spontaneously transform to monoclinic. This transformation is accompanied by 5% volume expansion which develops hydrostatic stress if the surrounding matrix is rigid. Moreover it increases the critical size for tetragonal phase stabilization in domains of aggregated nanocrystallites as large as 190 nm [203]. However, the introduction of non-hydrostatic strain energy reduces the critical size for tetragonal phase stabilization at room temperature [203].

The five different polymorphs of zirconia namely monoclinic, tetragonal,
cubic and orthorhombic -I and -II have different densities. Since the density of monoclinic structure is lower than that of tetragonal / cubic / orthorhombic [227], it can be converted to denser structure by applying an external hydrostatic pressure. From reports [228] it is found that on applying an external pressure within the range 2.2-15 GPa or greater, the monoclinic structure can be converted into orthorhombic structure. Tetragonal phase stabilization is possible in the temperature range 500-600 °C along with application of external pressure. In the case of nanocrystallites of size less than 10 nm, the surface energy difference overcomes the volume free energy difference of the involved phases and consequently the tetragonal phase which have lower surface energy than monoclinic phase can be stabilized without applying external pressure. In such nanocrystallites, the equivalent hydrostatic pressure would be acting internally on the particle surface to stabilize the tetragonal phase at room temperature. Calculation of internal hydrostatic pressure based on Gibb’s - Thompson equation [229] shows that its magnitude increases with decreasing nanocrystallite size. Calculations show an internal hydrostatic pressure of 20 GPa in ZrO₂ nanocrystallites of size 1 nm [145]. For nanocrystallites of size > 10 nm, the volume energy difference overcome the surface energy and as a result the monoclinic structure becomes more stable above 10 nm [209]. Moreover for strain free nanocrystallites of size greater than 10 nm, external pressure is required to stabilize tetragonal phase. The magnitude of external hydrostatic pressure increases linearly with crystallite size in the range 10 - 20 nm. But for nanocrystals above this size, the rate of increase in external hydrostatic pressure decreases with increase in crystallite size of zirconia [226]. In addition to critical size, the temperature also determines the magnitude of hydrostatic pres-
sure required to stabilize the tetragonal phase. At a given temperature, higher magnitude of external hydrostatic pressure is required to stabilize tetragonal phase in larger grain size zirconia [226].

Nanocrystalline zirconia powder obtained through wet synthesis technique is amorphous in nature. On thermal treatment at lower temperature, the tetragonal / monoclinic phase evolves from the initial amorphous phase based on the structural similarity between the evolving phase and amorphous phase. Livage et al. [230] studies demonstrates that tetragonal phase evolves from the amorphous dried zirconia powder provided the interatomic distance between Zr-Zr (0.22, 0.33, 0.37, 0.47 and 0.60 nm) is exactly the same as that of Zr-Zr interatomic distances corresponding to (111) plane of tetragonal phase. Besides the tiny tetragonal nanocrystallites of size 1.5 - 3.0 nm act as nuclei for the topo tactic crystallization of tetragonal phase from amorphous zirconia due to structural similarity [160]. In contrast to this, there are other reports [231, 232] which support the structural similarity between amorphous and monoclinic zirconia. The studies reveals that Zr-O and Zr-Zr interatomic distances in the amorphous gels are quite closer to the respective interatomic distances in monoclinic zirconia than tetragonal one. On comparing the studies whether the local ordering in the dried amorphous zirconia resembles monoclinic or tetragonal structure, it is clear that evolution of tetragonal phase from its dried as-synthesized amorphous powder on thermal treatment at low crystallization temperature is governed by various factors like nanocrystallite size, their aggregation tendency, surface or interfacial energies, hydrostatic and non-hydrostatic lattice strains, and external or internal hydrostatic pressure.

Apart from thermodynamic and strain energy, there exist another mech-
anism which predict the stabilization of tetragonal phase based on diffusion of oxygen into the zirconia lattice. This is quite similar to the stabilization of tetragonal phase in bulk zirconia by introducing oxygen vacancies into the zirconia lattice at higher temperature, or in vacuum, or by doping trivalent impurities at high temperature. In the case of nanocrystalline zirconia, the oxygen vacancies generated due to its crystallite size at nanoscale stabilize the tetragonal phase at room temperature. Studies reveal that structure of tetragonal nanocrystalline zirconia stabilized at room temperature through introducing oxygen vacancies is quite similar to the high temperature undoped tetragonal zirconia as well as doped room temperature tetragonal zirconia. Pioneer works by Srinivasan et al. [233] established that generation of anionic oxygen vacancies stabilizes the tetragonal phase of zirconia at room temperature and oxygen adsorption during thermal treatment triggers the tetragonal to monoclinic phase transformation. Similar reports by Osendi et al. [234] suggested that stabilization of tetragonal phase zirconia is favored by the existence of anionic (oxygen ion) vacancies with trapped electrons. Higher calcination temperature leads to particle coarsening which removes the defect centres and cause gradual transformation of tetragonal to monoclinic phase. Besides, the generation or elimination of oxygen ion vacancies in zirconia lattice under reduced or high oxygen partial pressure depends on processing time and the nature of chemical reactions involved [235]. Consequently the increase/decrease in density of oxygen of ion vacancies determines the percentage of monoclinic-to-tetragonal or tetragonal to monoclinic phase transformation. However in the absence of reduced oxygen partial pressure conditions, the generation of oxygen ion vacancies can be made possible through ‘nanoparticle size effect’.
Liu et al. [236] investigated the nanoparticle size effect on oxygen ion vacancy and found that zirconia powders with very small nanocrystallite size and high specific surface area possess excess oxygen ion vacancies. Owing to the high specific surface area of nanocrystalline powders, a major portion of the total atoms resides on the surface. As a result a large number of Zr-O bonds become weaker which leads to desorption of oxygen ions from zirconia lattice. This generates a large number of oxygen ion vacancies in the lattice with reduction in nanocrystallite size. Thus the presence of excess oxygen ion vacancy concentration in nanocrystallites with size less than 10 nm is responsible for the tetragonal phase stabilization in nanocrystalline ZrO$_2$ [237].

The present chapter investigates the influence of calcination temperature on tetragonal to monoclinic phase transformation in surfactant capped HAZ. These polymeric sheets are formed by hydrolysis (pH 9) and polymerization of surfactant capped zirconia tetramers [Zr$_4$(OH)$_8$(H$_2$O)$_{16}$]$^{8+}$ in aqueous solution. During polymeric sheet formation the hydrolysis of tetramers takes place with OH$^-$ ions released by NH$_4$OH which leads to the formation of hydrolyzed tetramers [Zr$_4$(OH)$_{16}$(H$_2$O)$_8$]. Two of these tetrameric unit condense and form a third unit which undergoes further condensation resulting in the formation of two dimensional sheets of Zr(OH)$_{4-x}$H$_2$O with water molecule and hydroxyl groups at the edges of the sheet [170]. The polymerized sheets connect together through condensation of hydroxyl groups resulting in hydrous amorphous zirconia with fluorite structure having surface water and hydroxyl groups. Moreover, in surfactant assisted precipitation method, the direction and growth of polymeric sheets are determined by nature of stabilization of surfactant capped zirconia tetramers in aqueous solution. In the case of stronger
surfactant stabilization, well-ordered polymeric sheets will be formed due to slow hydrolysis and polymerization of zirconia tetramers. However, for weak stabilization, the polymerization occurs randomly in many directions due to hydrolysis at a faster rate and hence the sheets condense randomly. The direction and arrangement of hydrolyzed zirconia tetramers in polymeric sheets determines the structure of zirconia nanoparticles obtained on thermal treatment of hydrous amorphous zirconia. The thermal treatment (at low crystallization temperature) of well-ordered polymeric sheets leads to the formation of tetragonal zirconia nanoparticles. However, the randomly ordered polymeric sheets crystallize into monoclinic zirconia. This is confirmed form the XRD of PVP (/CTAB) capped HAZ thermal treated at different temperatures (Fig. 4.1).

During thermal treatment dehydroxylation of surfactant capped HAZ takes place. At a given calcination temperature, the amount of dehydroxylation of PVP (/CTAB) capped HAZ depends on its degree of stabilization. PVP being a neutral polymer direct the polymerization of zirconia tetramers to take place in a well-ordered pattern through its steric action than CTAB. As a result Zr-OH-Zr is tightly bound and this lowers the dehydroxylation rate of PVP capped HAZ which is confirmed from TGA. Well-ordered polymeric sheets of \([\text{Zr}_4(\text{OH})_{16}(\text{H}_2\text{O})_8]\) on calcination yields zirconia nanoparticles with greater amount of tetragonal content. At temperature greater than surfactant decomposition temperature, the Zr-OH-Zr bond breaks which loosens the sheets, and grains coalesce leading to the transformation of tetragonal to monoclinic. During this process, the volatile products of surfactant degradations slow-down the rapid phase transformation from tetragonal to monoclinic. The volatile products formed during degradation of PVP (/CTAB) capped HAZ samples cal-
cined at 500, 600, 700 and 800 °C are identified from FTIR spectra (Fig. 4.3a and 4.3b). FTIR spectra of all PVP samples exhibited vibrational bands at 400-800 cm\(^{-1}\) and \(\sim 3420\) cm\(^{-1}\) attributed to Zr-O bond and stretching of hydroxyl ions formed at defect sites respectively. The PVP samples thermal treated at temperature greater than 526 °C showed vibrational bands corresponding to volatile products of PVP. For instance sample calcined at 600 °C shows vibrational band at 1750 cm\(^{-1}\) which is attributed to carbonyl stretching of five member mono-substituted lactam structures. This band confirms the formation of pyrrolidone on thermal degradation of PVP [207, 208]. The spectrum also shows a band at 1452 cm\(^{-1}\) which is attributed to C-H bending vibration from methylene group. Hence the presence of aliphatic compounds formed due to breaking of N-C linkage which is weaker than C-C, C-O and C-H is explicit. This confirms the release of pyrrolidone as the main product during the initial stage of PVP degradation.

Further on increasing the calcination temperature from 700 to 800 °C, the band at 1750 cm\(^{-1}\) disappeared and new band appears at 2800 - 3000 cm\(^{-1}\) region ascribed to C-H stretching vibration of aliphatic compounds confirming the formation of polygenic sequence. The band at 2351 cm\(^{-1}\) for sample calcined at 700 °C corresponds to absorption of CO\(_2\) evolved during oxidation of polygenic sequence formed by side substituents of PVP released during its degradation. In brief, from the FTIR spectra of PVP samples calcined at 500, 600, 700 and 800 °C, it is found that thermal degradation of PVP starts in the range 600-700 °C with the release of pyrrolidone as the main product. Subsequently when the sample is calcined at 800 °C, volatile products like hydrocarbons are formed due to thermal degradation of polygenic sequences. This
confirms that increased monoclinic content of sample calcined at 800 °C is due to degradation of polymer into volatile compounds and the steric stabilization ceases. This enhances the coalescence between the tetramers and lowers the surface energy for monoclinic phase.

On thermal treatment, the CTAB \(((\text{C}_{16}\text{H}_{33})\text{N(}\text{CH}_3)_3\text{Br})\) capped on HAZ sample starts to decompose at 458 °C and the complete decomposition depends on its interaction with nanoparticles. Samples calcined at 500-800 °C shows bands in the range 1300 - 1680 cm\(^{-1}\) correspond to CH\(_2\) scissoring and O-H bending mode of water around the bound head group of CTAB. The intensity of bands subsequently reduced with temperature due to removal of surface hydroxyl groups. Further, only samples calcined at 500-700 °C exhibits vibrational band at ~ 2850 and ~ 2920 cm\(^{-1}\) ascribed to C-H stretching and anti-stretching modes of hydrocarbon tail bound to the surface of nanoparticles respectively. This band disappears completely at 800 °C. However the vibrational band ~ 1627 cm\(^{-1}\) is still present with reduced intensity. Thus FTIR analysis confirms that for samples calcined at 500 °C the decomposed CTAB by-products interacts with surface of nanoparticles and subsequently decreased with temperature due to decomposition of CTAB. Hence the FTIR results confirm that thermal degradation of surfactant with temperature can cause a significant change in structure of zirconia nanoparticles. Further Raman spectra (Fig. 4.4) of samples thermal treated at different temperatures too support that surfactant determines the structure of HAZ which in turn decides the phase of zirconia nanoparticles. The PL spectra of thermally treated zirconia samples confirm the presence of significant tetragonal content.
4.5 Conclusion

This chapter describes the mechanisms underlying the structural transformation of HAZ obtained via surfactant assisted chemical precipitation technique on annealing. The polymeric sheet HAZ is formed by polymerization of surfactant capped hydrolyzed tetramers. The surfactant regulates the polymerization rate of tetramers and thereby determines the structure of HAZ. PVP through its steric action lowered the polymerization rate significantly than CTAB and consequently PVP capped HAZ is well-ordered than the CTAB one. The well-ordered sheet on thermal treatment at lower crystallization temperature resulted in zirconia nanocrystals with dominant tetragonal phase. Further in well-ordered sheet of HAZ, the dehydroxylation rate of Zr-OH-Zr is lower. However at higher calcination temperature, Zr-OH-Zr breaks and enhances the phase transformation from tetragonal to monoclinic. Further the by-products formed on thermal degradation of surfactant also control the phase transformation.