UNUSUAL PHASE TRANSFORMATION BEHAVIOR OF AMORPHOUS ZIRCONIA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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BACHELOR OF TECHNOLOGY
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CERAMIC ENGINEERING

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CERTIFICATE

This is to certify that the thesis entitled, "**Unusual phase transformation behavior of amorphous zirconia**" submitted by Miss **Dimple Pradhan** in partial fulfillments for the requirements for the award of **Bachelor of Technology** Degree in **Ceramic Engineering** at National Institute of Technology, Rourkela is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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CONTENT

Abstract

As-prepared amorphous zirconia (ZrO_2) powders synthesized through different solution route were crystallized with increase in calcination temperature. Generally, the phase transformation from amorphous nature to crystalline forms of ZrO_2 was at around 450 °C, which was confirmed from the thermal analysis. After this phase transformation, tetragonal ZrO_2 slowly convert to monoclinic phase of ZrO_2 at higher temperature. The crystallization temperature of amorphous to tetragonal was affected by processing parameters like pH and temperature and reacting agents.

The aim of the work is to shift the phase transformation behavior of tetragonal zirconia to high temperature so that zirconia should retain amorphous upto that temperature.

The present work deals with a novel synthesis route for synthesizing amorphous zirconia (a-ZrO_2) upto700 °C. In this work, a-ZrO_2 and nanocrystalline tetragonal zirconia (t-ZrO_2) were synthesized through both reduction route using sodium borohydride ($NaBH_4$) and hydrolysis route using ammonium hydroxide (NH_4OH). The synthesis has been carried out by maintaining at a constant pH (≈11). An unusual phase transformation behavior of a-ZrO_2 into a nanocrystalline t-ZrO_2 was observed at above 900 °C in case of reduction route. Amorphous ZrO_2 was used for high k-gate dielectric application due to its thermodynamically stable in contact with Si-single layer structure and its excellent reliability. Here, in this work, a-ZrO_2 has been successfully synthesized and that remains amorphous upto 700 °C. Above 700 °C, a-ZrO_2 slowly transformed into t-ZrO_2 and that remains stabilized upto 900 °C. Thermal, structural, microstructural and IR characterization have been studied for analyzing the a-ZrO_2 as well as crystalline t-ZrO_2.

Technologically, if one can make amorphous ZrO_2 thin film which remains amorphous upto at least 800 °C could be a very useful material for electronic industries.

CHAPTER 1

GENERAL INTRODUCTION

1.1 INTRODUCTION

Zirconia is a remarkable material, which has attracted a great deal of attention from scientists, technologists and researchers. It is one of the most widely studied materials in the aspects of mechanical, structural and electrical properties. It is well known for good wear resistance, hardness, low coefficient of friction, chemical inertness, elastic modulus ionic conductivity, low thermal conductivity and high melting temperature that make it attractive as an engineering material. Due to the above mentioned properties zirconia is used as extrusion dies, machinery wear parts and piston caps. In addition, they are applied in electrochemical cells (fuel cells, oxygen sensors, oxygen pumps, etc.) due to their high oxygen-ion conductivity at elevated temperature. Its low thermal conductivity has allowed its use for thermal barrier coatings for aerospace engine components. While refractory applications represent the tonnage usage of stabilized Zirconia it is also used as a glower for incandescent lighting. Industrial application of Zirconia has been increased after the discovery of the concept of transformation toughening. Much progress regarding transformations and processing is due to the detailed crystal structure analyses of the various phases of Zirconia. In addition to that amorphous zirconia is used as a catalyst in various reactions and it is an important high-K dielectric material that is being investigated for potential applications as an insulator in transistors in future nanoelectronic devices.

1.2 OCCURRENCE

The two main source of Zirconia are baddeleyite (impure monoclinic Zirconia) and Zircon, ($ZrSiO_4$) which occurs as secondary deposits in Kerala, Florida and South Africa. It is frequently mixed in sand with other minerals like rutile and monazite. Baddeleyite is found in smaller deposits and usually contain contaminants such as silica and iron oxide.

1.3 DIFFERENT POLYMORPHS OF ZIRCONIA

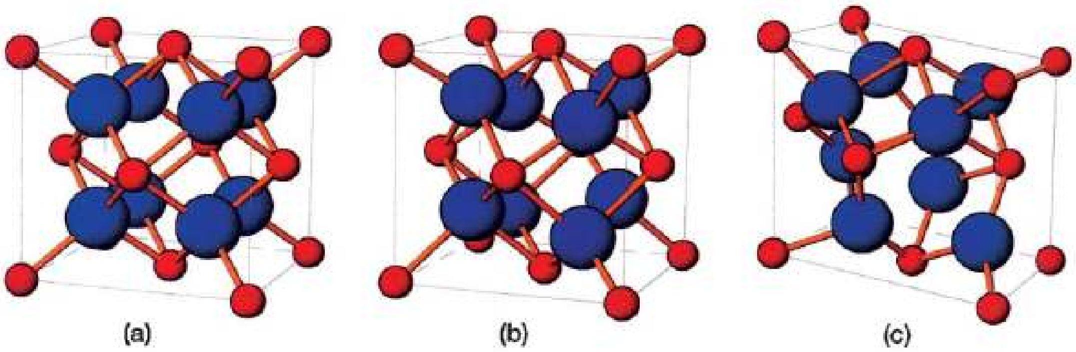


Fig. 1.1 Schematic representation of the three polymorphs of ZrO2: (a) cubic, (b) tetragonal, (c) monoclinic.

The ZrO_2 exists in three polymorphs: cubic (c), tetragonal (t) and monoclinic (m) at various temperature ranges.

Cubic

The cubic phase which is stable from 2370^0C to melting point was detected by Smith and Cline by high temperature XRD. It has a fluorite type crystal structure in which each Zr is coordinated by eight equidistant oxygen atoms and each oxygen is tetrahedrally coordinated by four zirconium.

Tetragonal

The tetragonal phase is stable between 1100^0C to 2370^0C.In this phase the Zr is surrounded by eight oxygen atoms four at a distance of 0.2455 nm and the other four at a distance of 0.2065 nm.

Monoclinic

The monoclinic phase is thermodynamically stable upto 1100^0C.The crystal structure of monoclinic was determined by XRD by McCullough and Trueblood and others. The main features of the structures are (a) sevenfold coordination of Zr with a range of bond lengths and bond angles. (b) layers of triangularly coordinated OI-Zr and tetrahedrally coordinated OII-Zr.(c) Zr atoms are located in layers parallel to the (100) planes separated by OI-OII atoms on either side (d) the thickness is wider when Zr atoms are separated by OI atoms than separated by OII atoms.

1.4 PHASE TRANSFORMATIONS

The monoclinic phase exists upto 1100^0C and the tetragonal phase exists in the temperature range of 1100^0C-2370^0C and the cubic phase is found above 2370^0C.The thermal expansion of monoclinic ZrO_2 is strongly anisotropic. On heating it is associated with substantial amount of contraction and on cooling the $t \rightarrow m$ transformation occurs at 900^0C and is accompanied by the directional 5 % increase in volume. This transformation monoclinic to tetragonal or vice versa is also termed as martensitic transformation. A similar transformation occurs in metal like steel .It is a diffusionless transformation.ZrO_2 has thermal expansion coefficient and elastic modulus similar to steel .Hence Zirconia is also called “Ceramic Steel”.

1.5 STABILIZATION OF ZIRCONIA

By addition of dopants

All engineering applications require the structure to be stabilized. Addition of CaO, MgO, Y_2O_3 and other rare earth element oxides can lower the transition temperature and we can obtain the stabilized phase i.e. tetragonal and cubic at lower temperature. The phase diagrams of binary oxides systems show that partially stabilized Zirconia (PSZ) occurs

(a) When the dopant is present in a concentration less than that needed for complete stabilization.

(b) When the fully stabilized cubic Zirconia with suitable solute content is heat treated under appropriate conditions of temperature and time. The incorporation of these oxides not only lower the transition temperatures but also decreases the linear thermal expansion coefficient of the two phase material as also volume change is associated with the phase change that takes place. Stabilization of cubic and tetragonal forms is gaining importance because of its excellent mechanical properties like high strength and toughness and oxygen conductivity. There are many factors which need to be controlled in order to increase the stabilization of the tetragonal and cubic phase relative to the thermodynamically stable monoclinic phase at room temperature. Factors important to obtain stabilization are type and amount of stabilizing agents, particle size, and heat treatment temperatures homogeneous composition and low agglomeration. Stabilization of metastable phases also depends on crystallite size and on the process of preparing the powders.

1.6 SIGNIFICANCE OF NANO

Reducing the size of the crystals can have quite dramatic effect on the properties of bulk materials particularly increasing strength. When the grain size moves to nanoscale the ceramics become more ductile. There is reduction in brittleness which is a major problem in ceramic materials. Nanomaterials show enhanced properties due to higher surface energy and surface area.

Apart from addition of stabilizers the retention of tetragonal phase is possible if the particle size is below some critical value primarily due to a high surface energy. The significance of tetragonal phase is that the transformation toughening mechanism depends on the tetragonal phase present. In addition to that the nanocrystallites are believed to have improved chemical and physical properties as compared to larger sized particles.

1.7 TRANSFORMATION TOUGHENING

It is one of the properties that involve control of composition and manipulation of microstructure. Zirconia is a material that undergoes a change in the way its atoms are stacked at different temperatures (polymorphic transformation). Zirconia has the monoclinic crystal structure between room temperature and about 1100°C. Above 1100°C zirconia converts to the tetragonal crystal structure. This transformation is accompanied by greater than one percent shrinkage during heating and equivalent expansion during cooling. At a much higher temperature, the zirconia changes from tetragonal to a cubic structure. With proper chemical additions and heat treatments, a microstructure can be achieved during cooling that consists of lens-shaped “precipitates” of tetragonal zirconia in cubic grains of zirconia. Normally, the tetragonal material would transform to the monoclinic form during cooling, but it must expand to do so. The high strength of the surrounding cubic zirconia prevents this expansion, so the tetragonal form is retained all the way down to room temperature. As a result, each tetragonal zirconia precipitate is under stress. For each tetragonal precipitate if a crack tries to form then tetragonal precipitates next to the crack are now able to expand and transform back to their stable monoclinic form. This expansion adjacent to the crack presses against the crack and stops it. This is the mechanism of transformation toughening.

1.8 SYNTHESIS ROUTES

Precipitation technique

The precipitation method starts with the chloride form of the constituent, which is precipitated out of solution in their corresponding hydroxide form using NH_4OH as a reagent. Then the gel is washed with water preferably hot water for removal of chloride ions and then it is washed with ethyl alcohol and then dried at 110^0C . The advantage of the coprecipitation method is the constituents are mixed on the atomic level. This avoids contamination. Materials with more interesting properties, from the point of view of technological applications, are obtained at constant pH. Higher crystallinity, smaller particle size, higher specific surface area and higher average pore diameter are expected to be found for materials obtained by precipitation at constant pH, as compared to the materials obtained at variable pH.

Reduction technique

In this technique the precursor solution of Zirconium salt in aqueous medium is reduced using reagents like hydrazine hydride, sodium borohydride to produce Zirconia nanoparticles. The whole process was allowed to take place at a constant pH. Using this technique we have been able to retain t-ZrO_2 upto higher temperature than precipitation technique.

It is observed that when amorphous zirconia is heated it crystallizes in the metastable tetragonal phase and then transforms into stable monoclinic phase on further heating. In our work we want to retain the amorphous zirconia upto higher temperature so that correspondingly the crystallization temperature is shifted and we obtain the tetragonal zirconia upto higher temperature.

CHAPTER 2

LITERATURE REVIEW

2.1 Effect of pH, particle size and calcination temperatures on polymorphs of ZrO_2

R. Ramamoorthy et.al. (Journal of European Ceramic Society (1999) 19 1827-1833) observed that tetragonal or cubic phase stabilization and the associated phase transformations processes seem to depend on the grain size to a certain extent and more dependent on the chemical composition of the powders. He prepared nanocrystalline ZrO_2 powder by the method of hydrolysis of Zirconium oxychloride and neutralizing it with ammonia solution. The amorphous ZrO_2 crystallizes in tetragonal phase around 718k to 753k on heating. [1]

Keramidas et al. (Journal of American Ceramic Society 1974 57 22-24) have argued that in reality, the amorphous ZrO_2 is a bulk sample of crystal nuclei of structure very similar to that of the tetragonal ZrO_2 but with very limited long range periodicity. These nuclei serve nuclei serve as nuclei for the growth of metastable tetragonal ZrO_2 when the specimens are heated. On heating the sample through a diffusionless transformation the inter-atomic distances change enough for the metastable tetragonal phase to be formed. [2]

A.Shrivastava et al.(Material Letters Volume3,number5) prepared Zirconium citrate using Zirconium oxychloride and citric acid. The XRD studies showed that powder prepared by this method is tetragonal upto 600^0C after which it progressively transforms to monoclinic. Beyond 800^0C the phase is completely monoclinic.[3]

Bussarin Ksapabutr et al. (Powder Technology 148 (2004) 11-14)prepared zirconia powders by sol gel method using sodium glycozirconate complex. The resulting Zirconia was characterized using XRD based on which the first crystalline structure developed from the amorphous phase was the tetragonal polymorph, which was formed between 500^0C and 800^0C. [4]

Jiahe Liang et al. (Material Science Bulletin 38 (2003) 161-168) reported preparation of nanoscale hydrous zirconia dioxide by ultrasonication technique. The tetragonal phase of Zirconia was observed after amorphous product is heated around 300^0C for 2 hrs. Thus, here the stabilized tetragonal zirconia is produced at low temperature. [5]

M.Tahmasebpour et al. (Journal of the European Ceramic Society 28 (2008) 773–778) produced pure monoclinic zirconia powder by polyacrylamide gel method. The XRD patterns of the synthesized product with oxynitrate salt are shown to have amorphous structure at 300◦C. By rising the calcination temperature, a semicrystalline structure (only tetragonal phase) is formed at 400◦C. As the calcination temperature increases to about 600◦C, both monoclinic and tetragonal phases are detected. Further increasing of the temperature, causes an increase in the proportion of monoclinic phase and at temperature 800◦C the transformation to monoclinic phase is completed. [6]

M Rezaei et al. (Powder Technology 168 (2006) 59–63) produced nanocrystalline zirconia powder with high surface area, pure tetragonal phase and mesoporous structure by a surfactant-assisted route in which the precursor solution was zirconium nitrate to which ammonia solution was added dropwise by using Pluronic P123 block copolymer as the surfactant. The DTA curve shows an exothermic peak at 610^0C usually known as "glow exotherm" is attributed to crystallization of amorphous Zirconia. [7]

J.A Wang et al. (Catalysis Today 68 (2001) 21–30) made a comparative study of zirconia powders synthesized by solgel and coprecipitation technique .For the powder prepared by precipitation technique the crystallization temperature is 470^0C shown by DTA. Also there exists an additional phase with zirconia at that temperature so based on the XRD analysis, we ascribed this phase to a quasi-amorphous tetragonal phase produced in the decomposition process of $Zr(OH)_4$ whereas in sol gel method ZrO_2 crystallization occurs around 650^0C. [8]

M.M Rashad et al. (journal of materials processing technology 195 (2008) 178–185) prepared ZrO_2 nanopowders via three processing routes: precipitation (CP), citrate gel combustion (CGC) and microemulsion refined precipitation (MRP). The change in processing routes at different thermally treated temperatures from 120 to 1200 ◦C led to the change of polymorphic phases and properties of the produced ZrO2 nanopowders. Precursors derived from these three processing routes exhibited very different formation temperature for ZrO_2 phases. Directly precipitated precursor and the citrate ZrO_2 precursor were given tetragonal ZrO_2 phases at 700 ◦C which inverted to monoclinic ZrO_2 phase at 1000–1200 ◦C. On the other hand, MRP technique gave tetragonal ZrO_2 phase at 500–700 ◦C and cubic ZrO_2 phase at 1000–1200◦C. Amorphous ZrO_2 was converted to tetragonal phase at low temperatures for all synthesis techniques and the tetragonal phase is transformed to cubic or monoclinic phase by increasing the temperature, depending on the particular kinetic conditions and chemical environments. The morphology of zirconia particles was affected by synthesis routes and thermally treated temperature. [9]

Mondal et.al [A. Mondal, S. Ram, J. Am. Ceram. Soc., **87**, 2187 (2004)] have synthesized monolithic t-ZrO_2 nanopowders with an amorphous $ZrO(OH)_2$.xH2O polymer precursor by using NH_4OH .The final pH of the solution was nearly 10.It has been observed that the polymer precursor solution has thermal decomposition in self stabilized t-ZrO_2 nanoparticles (size 8nm) at temperature as low as 2000C.The particles grow no larger than 12 nm at 600^0C with the presence of 10% m-phase and 90% t-phase of ZrO_2.Pure m-ZrO_2 appears with a sudden growth of size 22nm at a temperature 800^0C.Quantitatively ,a high level of oxygen vacancies and manifested grain surface seem to determine the metastable t-ZrO_2 structure in small crystallites. [10]

B. B. Nayak .et al [AIP Conf. Proc., 1063, 206 (2008)] synthesized ZrO_2 nanoparticles by chemical reduction of zirconium salt in an aqueous medium with sodium borohydride ($NaBH_4$) as a reducing agent, at two different pH of 3.0 and 8.7. The crystallization peak occurs at the temperature range of 400 °C to 600 °C. Pure t-ZrO_2 nanoparticles with crystallite size as small as 7 to 8 nm resulted on heating the amorphous as-prepared precursor powders at 600 °C. The t--> monoclinic (m) phase transformation occurred at 800 °C as the crystallite size increases to 30 nm. This is a novel technique for stabilizing the t-phase of ZrO_2 at moderate temperature for different applications. [11]

Jack C. Lee Microelectronics Research Centre, The University of Texas at Austin investigated amorphous ZrO_2 and HfO_2 for dielectric applications. The thin film remained amorphous upto at least 800^0C.It is used as an insulator in transistors.

2.2 Objectives of the present studies

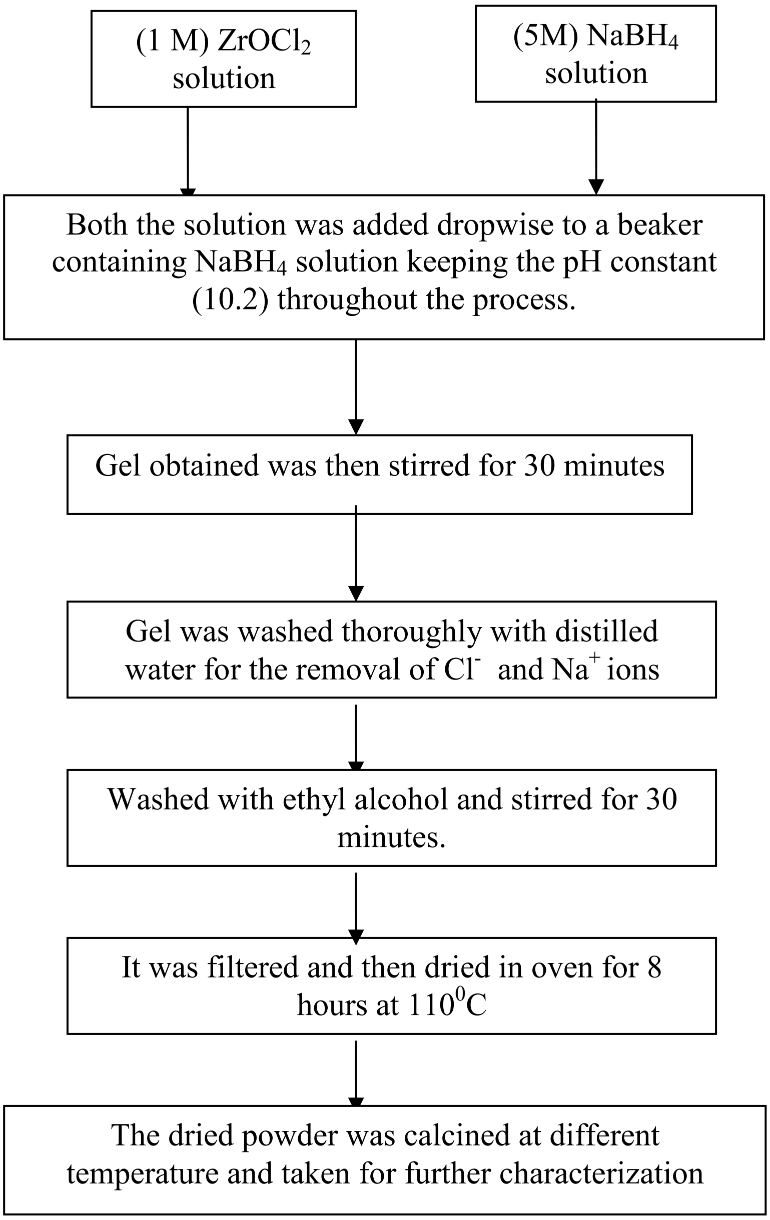
The main objectives of the present studies are:

- To shift the phase transformation behavior of tetragonal zirconia to high temperature so that amorphous zirconia retains amorphous upto that temperature.
- To analyze the stabilization behavior of metastable t-ZrO_2 by varying the concentration of $NaBH_4$ and calcination temperature by maintaining a constant pH of around 10.2.
- Study and compare the thermal, structural, microstructural and IR result of the as prepared ZrO_2 powder as well as calcined zirconia.

CHAPTER 3

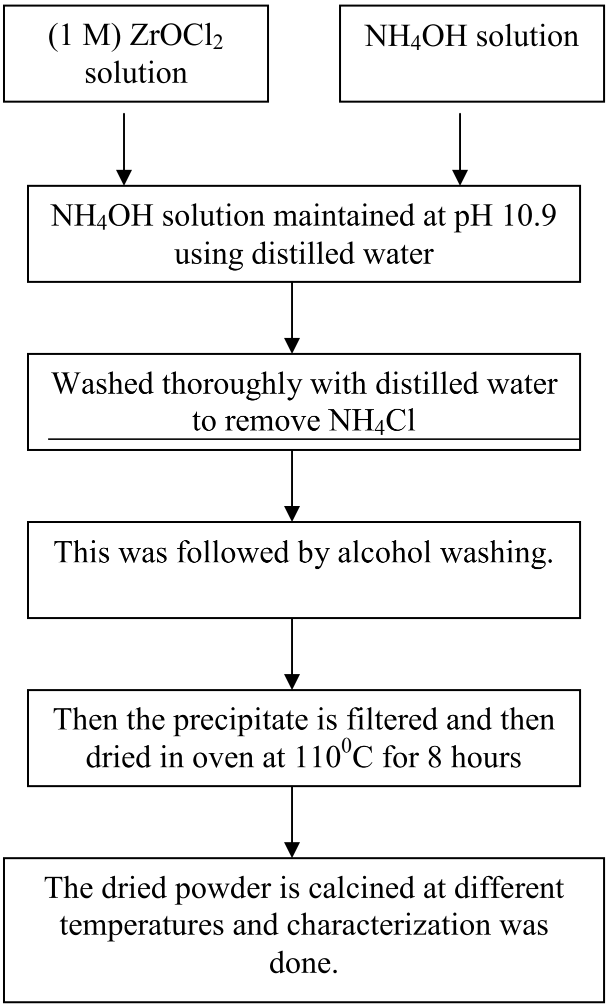
EXPERIMENTAL WORK

3.1 Preparation of ZrO_2 using $NaBH_4$



A batch of Zirconia gel was prepared through reduction technique by using $NaBH_4$. An Aqueous solution of 1M concentration $ZrOCL_2.8H_2O$ was prepared in a beaker from high purity salt by dissolving the salt in distilled water. $NaBH_4$ of concentration 5M was prepared in another beaker. Now we took about some $NaBH_4$ in beaker and two solutions both Zr salt and $NaBH_4$ was poured dropwise maintaining nearly constant pH.The final pH of gel was 10.2 .The gel obtained was washed thoroughly with water and then followed by alcohol washing. Then it was dried in oven at 80^0C for 24 hrs.The dried powder was grounded in agate mortar and calcined at different temperatures. A similar batch was prepared for 0.5M $NaBH_4$.

3.2 Preparation of ZrO_2 using NH_4OH



In order to make a comparative study another batch of Zirconia was prepared by precipitation technique .The precursor solution used was $ZrOCl_2.8H_2O$ which was precipitated using NH_4OH. Here about 25 ml of NH_4OH solution was taken in the beaker and pH was maintained at 10.9 by adding water. 1M Zr Solution was taken in a burette and NH_4OH Solution was taken in another burette. Then both the solutions were simultaneously added dropwise in the beaker maintaining a constant pH throughout as in the previous process the gel was washed repeatedly to remove Chloride ions and then dried and calcined at different temperatures.

3.3 General characterization

Thermal

Thermal decomposition of an amorphous ZrO_2 powder followed by its reconstructive nucleation of t-ZrO_2 nanoparticles were studied using differential scanning calorimetric and thermogravimetric (DSC-TG) by heating the sample at 10 °C/min in argon in a thermal analyzer (Netzsch, Germany).

X-ray diffraction

The phase identification and the crystallite size of the processed ZrO_2 nanopowders were characterized by Philips X-Ray Diffractometer PW 1730 with nickel filtered Cu K_ radiation (_ = 1.5406 A°) at 40 kV and 30mA. The crystallite sizes of ZrO_2 nanopowders were determined for the most intense peak (1 1 1) plane of ZrO_2 crystals from the X-ray diffraction data using the Debye-Scherrer formula corresponding to the full width half maxima of dominant peak:

$$D= k \lambda /\beta \mathrm{Cos}\theta$$

Where *D* is the crystallite size, *k* = 0.9 is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction plane, λ the wavelength of Cu target = 1.5406 Å, and θ is the Bragg angle.

The volume fraction of tetragonal (t) and monoclinic (m) phase present was calculated by using the formula:

$$V_m=1.311X_m / (1+0.311X_m)$$

$$X_m= [I_{(111)m} +I_{(111)m}]/ [I_{(111)t} + I_{(111)m} + I_{(111)m}]$$

Transmission Electron Microscopy (TEM)

The grain size, particle size and morphology were studied in Transmission Electron Microscope (TEM) (model: CM 200, Phillips). For preparation of TEM sample, the powder was dispersed in isopropyl alcohol in an ultra sonication bath (20 kHz, 500 W) for half an hour. One drop of the well-dispersed sample solution was deposited on to a carbon coated copper grid (400 mesh). The dried grid was used for microscopy

FTIR (Fourier Transformation IR spectroscopy)

FTIR spectra of the powders in KBr pellets were studied in the range of 450 – 4000 cm^{-1} by using IR-spectrometer.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes thermal, structural, microstructutral and infra-red analysis of ZrO_2 nanoparticles prepared through constant pH process using $NaBH_4$ NH_4OH.

4.1 Thermal behaviour of as-prepared ZrO_2

Figure 4.1 shows DSC/TGA data for as prepared powder of composition 1MZr solution and 5M $NaBH_4$ solution. An exothermic peak was obtained at 800 ^{0}C which corresponds to the crystallization of amorphous zirconia. Below 800^{0}C the powder is amorphous in nature. The TGA graph shows weight loss of 23.5%.

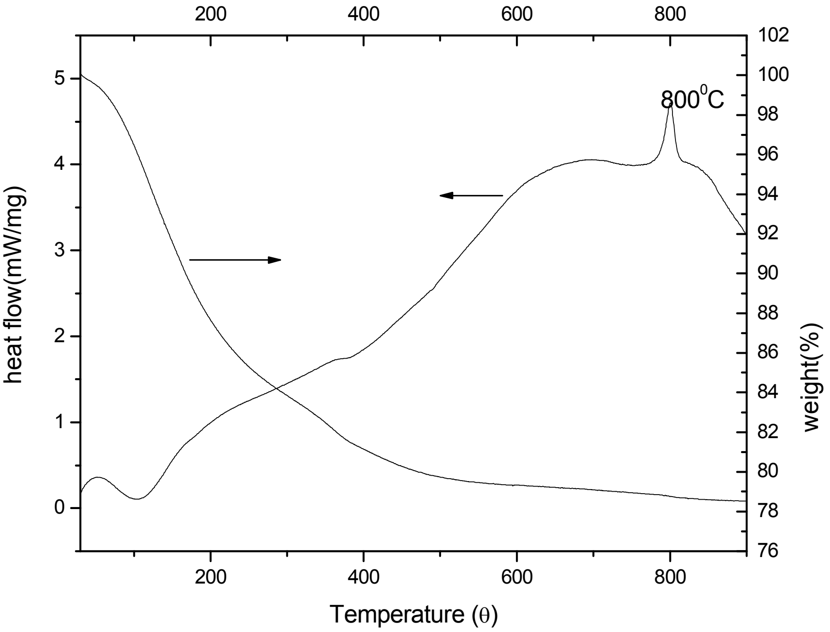


Fig. 4.1: DSC-TG plot of as-prepared zirconia synthesized using 1MZr solution and 5M $NaBH_4$ solution

Figure 4.2 shows a DSC/TGA plot of as prepared powder having composition 1M Zr Solution and 0.5M NaBH4 .Here a sharp exothermic peak is observed at 716 ^{0}C due to crystallization of amorphous Zirconia. The total weight loss observed is 19%.

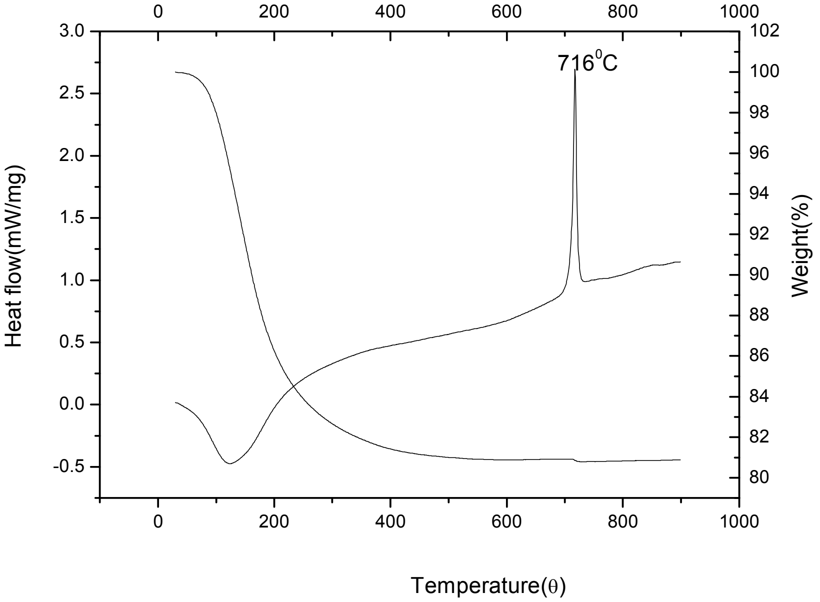


Fig. 4.2: DSC-TG plot of as-prepared zirconia synthesized using 1MZr solution and 0.5M $NaBH_4$ solution

On comparing the DSC/TG data plot Fig 4.1 (1M ZrO_2 and 5M $NaBH_4$) and Fig 4.2 (1MZrO_2 and 0.5M $NaBH_4$) we observe the first endothermic peak around (100^{0}C to 130^{0}C) on both graphs which may be accounted for evolution of absorbed water .Also we notice that former shows the crystallization peak at around 800^{0}C whereas the latter shoes the same around 716^{0}C.This shows that on increasing the concentration of $NaBH_4$ we can shift the crystallization peak and retain the tetragonal phase upto higher temperature.

Fig 4.3 shows the DSC/TGA plot for raw powder prepared via precipitation route having composition 1M Zr solution and NH_4OH.The crystallization peak was observed at around 462^0C.The total weight loss observed here is 18% which was calculated from the graph obtained by TGA.

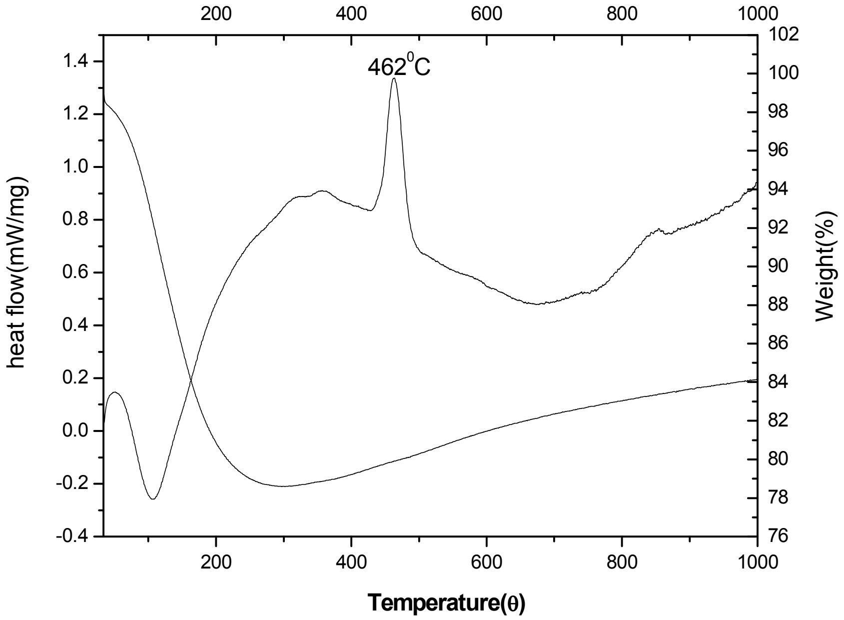


Fig. 4.3: DSC-TG plot of as-prepared zirconia synthesized using 1MZr solution and NH_4OH solution

If we compare the results obtained by precipitation technique using NH_4OH and Reduction technique using $NaBH_4$ we see that with the latter one crystallization of amorphous powder occurs at higher temperature.

4.2 Structure and microstructure

The XRD of ZrO_2 nanopowders prepared by reduction technique containing 1M ZrO_2 and 5M $NaBH_4$ calcined at different temperature 700^0Cand 800^0C with soaking period of 1 hr is shown in Fig.4.4. The XRD obtained at 700^0C/1hr shows the purely amorphous nature of powder and when we increase the calcination temperature to 800^0C/1hr we have obtained a wholly tetragonal phase.

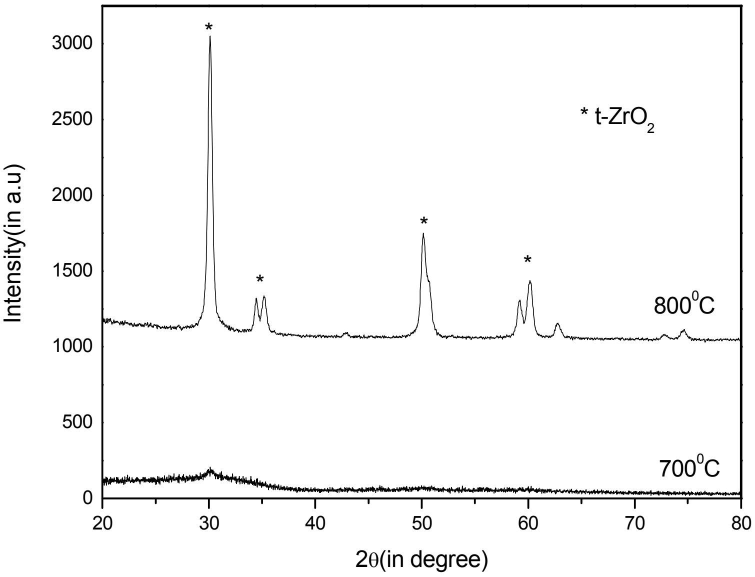


Fig. 4.4: XRD pattern of ZrO_2 powders synthesized using 1M Zr solution and 5M$NaBH_4$

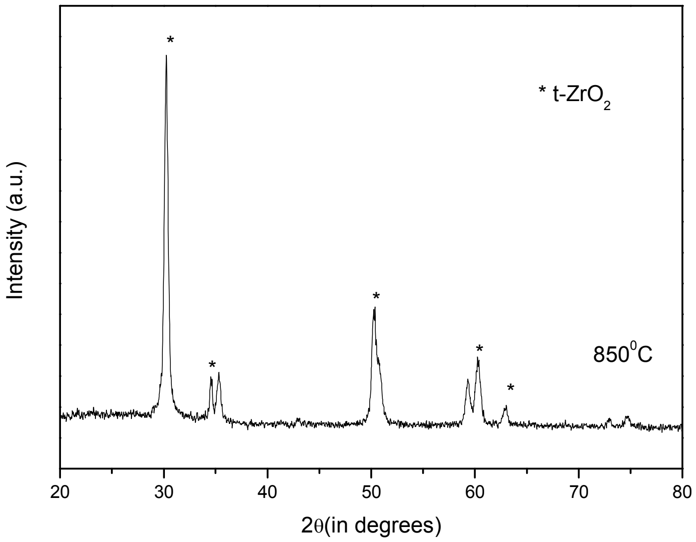


Fig. 4.5: XRD pattern of ZrO_2 powders synthesized using 1M Zr solution and 5M$NaBH_4$

The XRD pattern of ZrO_2 having composition 1M ZrO_2 and 5M $NaBH_4$ calcined at 850^0C is shown in Fig. 4.5 .The graph shows a purely tetragonal phase of Zirconia .

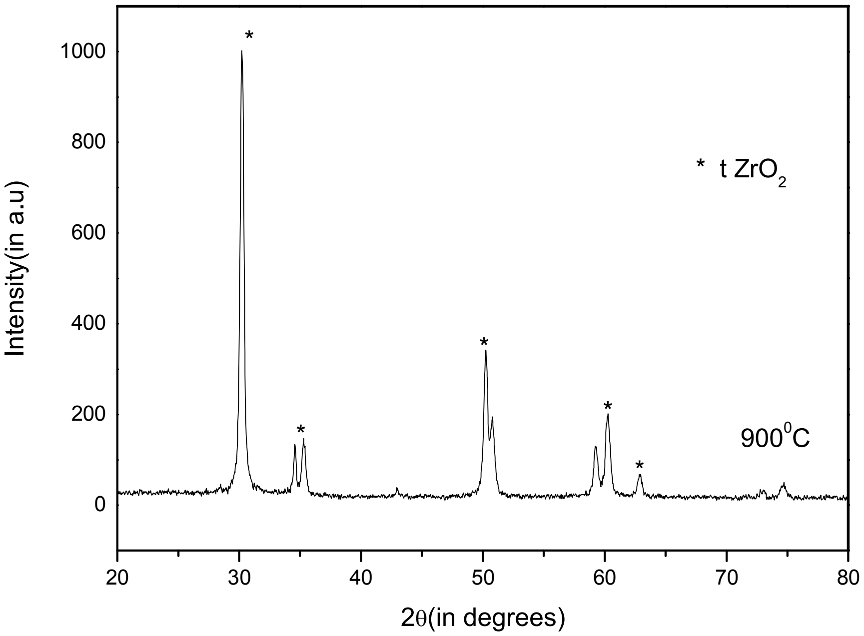


Fig. 4.6: XRD pattern of ZrO_2 powders synthesized using 1M Zr solution and 5M$NaBH_4$

The XRD Profile of ZrO_2 nanopowders calcined at 900^0C is shown in Fig. 4.6.The diffraction peaks are indexed as tetragonal and is in good agreement with the standard data file.

The crystallite size of the ZrO_2 nanopowders calculated from XRD analyses using Debye-Scherrer formula for the most intense peak (111) plane are given in Table 4.2:

Table 4.2: Crystallite size of ZrO_2 Powders calcined at different temperatures.

Temperature (^{0}C)	Crystallite Size (nm)
700	Amorphous
800	17
850	21
900	23

The XRD of ZrO_2 nanopowders prepared by reduction technique containing 1M ZrO_2 and 0.5M $NaBH_4$ calcined at different temperature 600 °C, 700^0Cand 800^0C with soaking period of 1 hr is shown in Fig.4.7. Amorphous nature was obtained upto 600 °C and XRD obtained at 700^0C/1hr shows the purely tetragonal nature of ZrO_2 and when we increase the calcination temperature to 800^0C/1hr we have obtained fully monoclinic along with minor tetragonal phase.

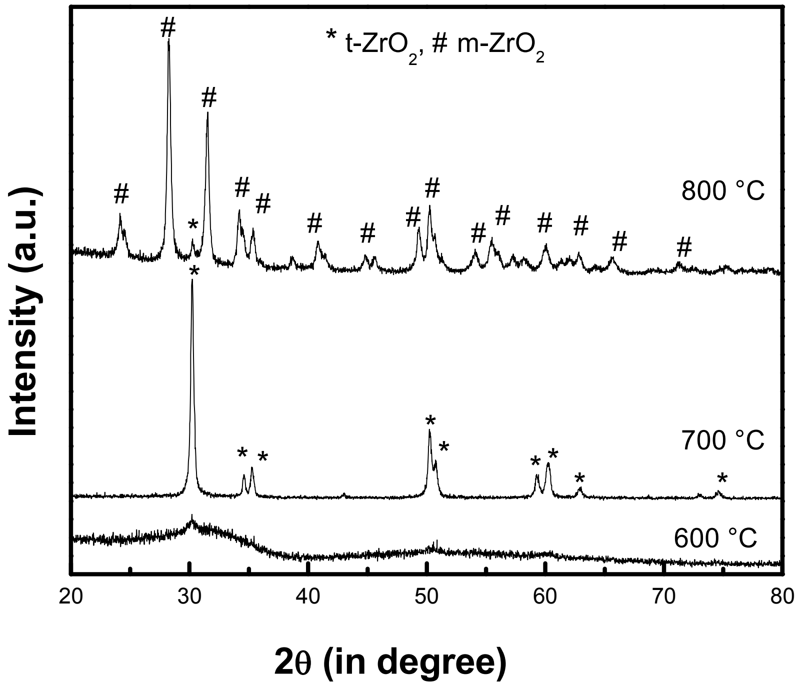


Fig. 4.7: XRD pattern of ZrO_2 powders synthesized using 1M Zr solution and 0.5M $NaBH_4$

The crystallite size(in nm) of the ZrO_2 nanopowders calculated from XRD analyses using Debye-Scherrer formula for the most intense peak (111) plane are given below in Table 4.1:

Table 4.2: Crystallite size of ZrO_2 Powders calcined at different temperatures.

Temperature(^{0}C)	Crystallite Size(nm)
600	Amorphous
700	23
800	23

The XRD pattern of ZrO_2 Powder prepared by precipitation route having composition 1M Zr solution and NH_4OH is shown in Fig. 4.8. The powders were calcined at 700^0C and 800^0C. At 700^0C the synthesized product shows a combination of monoclinic and tetragonal phase. Further increasing the calcination temperature causes an increase in proportion of monoclinic phase. The Crystallite size of samples was calculated by Debye Scherrer formula.

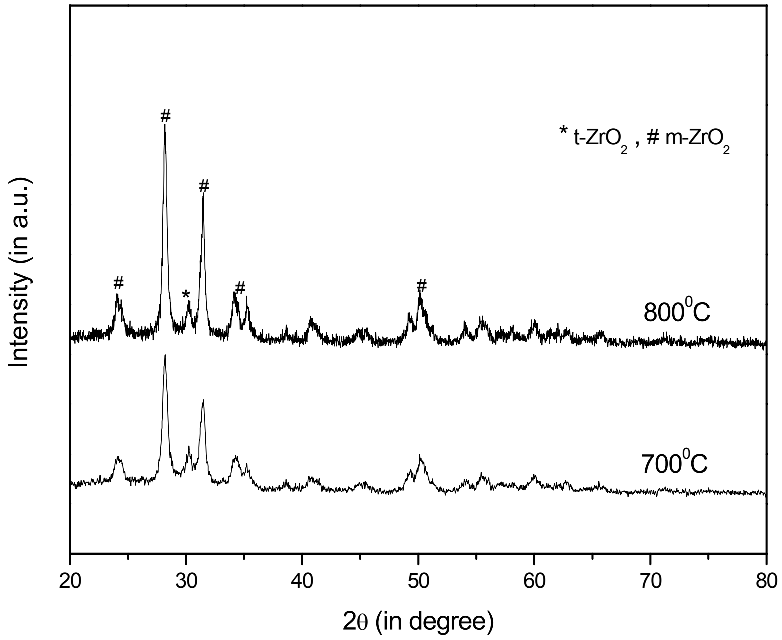


Fig. 4.8: XRD pattern of ZrO_2 powders synthesized using 1M Zr solution and NH_4OH

The crystallite size(in nm) of the ZrO_2 nanopowders calculated from XRD analyses using Debye-Scherrer formula for the most intense peak (111) plane are given below in Table 4.2:

Table 4.3: Crystallite size of nanopowders calcined at different temperatures.

Temperature(^{0}C)	Crystallite Size(nm)
700	17
800	21

For TEM of synthesized ZrO_2 nanopowders calcined at 700^0C/1hr the sample was first sonicated in isopropyl alcohol for about 15 minutes. Then a small amount of dispersed sample was taken with the help of a pipet and then a drop was allowed to fall on the small disc .The results of TEM is shown below.

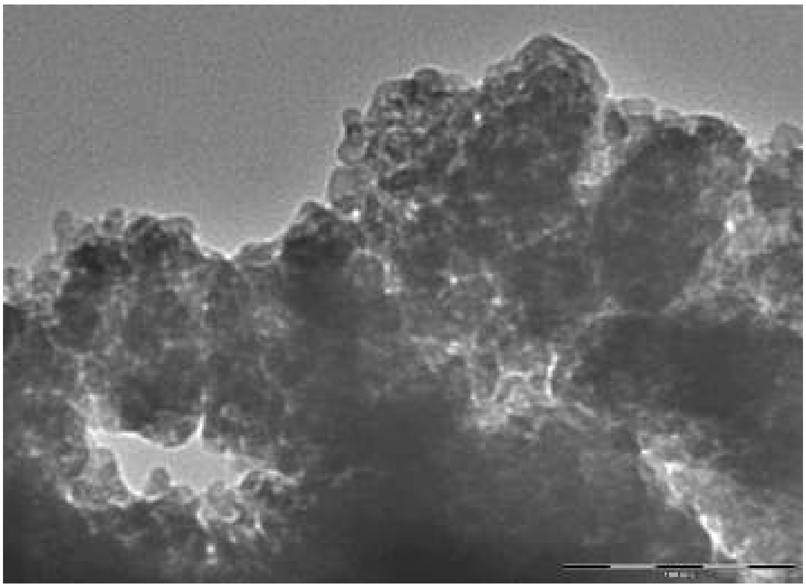


Fig. 4.9: TEM micrograph of amorphous zirconia

The diffraction pattern shows the presence of amorphous phase in the sample. This result is also supported by the XRD analysis of sample.

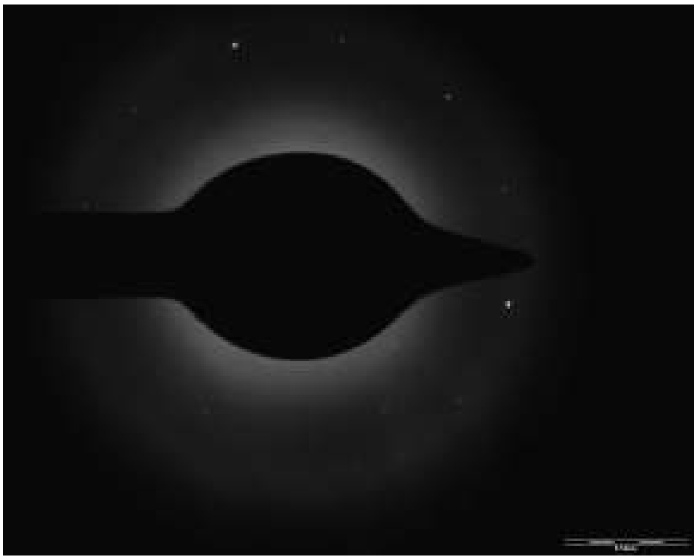


Fig. 4.10: Diffraction patterns confirms the amorphous nature of zirconia

4.3 IR spectra of as-prepared ZrO_2 powders

For ZrO_2 powders synthesized by 5M $NaBH_4$:

Infra-Red spectra in the range of 400 – 4000 cm^{-1} for as-prepared ZrO_2 powders and nanopowders calcined at 800^0C/hr synthesized using $NaBH_4$ was shown in Fig. 4.11 and Fig 4.12. Individual bands of the Zr-O group vibrations exist in both $ZrO_2.xH_2O$ and ZrO_2. Also O-H bending and stretching vibrations exist in $ZrO_2.xH_2O$ and H_2O molecule. The OH group is distinguished easily in H_2O molecule by its bending vibration which appears in a single band at ~1640 cm^{-1} that confirms the presence of water in the as-prepared powder. Another O-H bending vibrations in the hydroxyl group in the $ZrO_2.xH_2O$ molecule appears at ~ 1385 cm^{-1} and one asymmetric O-H stretching band occurs in H_2O in the range of 2929 to 3414 cm^{-1}. From the IR spectra, the as-prepared powders reveal that the ZrO_2 nano powders have significant amount of surface-adsorbed H_2O. The infrared characteristics bands observed in the as-prepared ZrO_2 nanopowders and those calcined at 800^0C/hr prepared through $NaBH_4$ are given in Table 4.4.

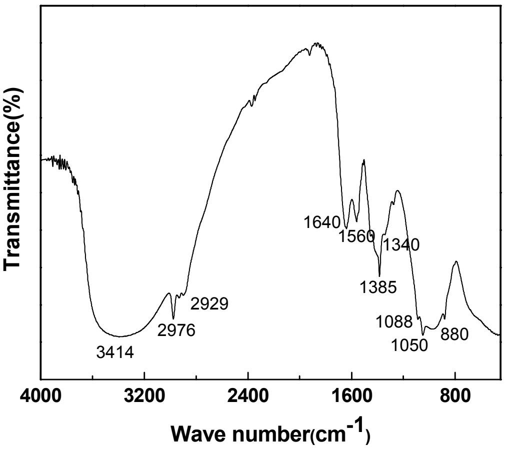


Fig. 4.11: IR spectra of as-prepared ZrO_2 powder synthesized from $NaBH_4$

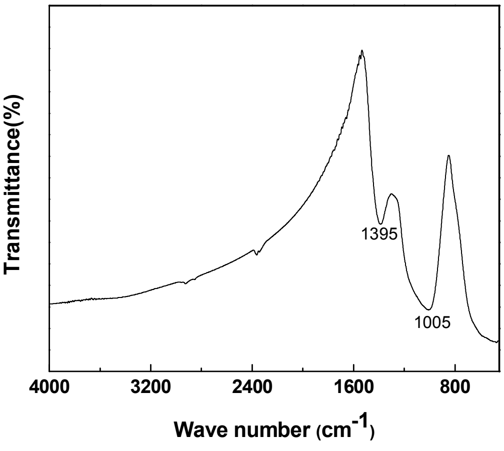


Fig. 4.12: IR spectra of ZrO_2 powder synthesized from $NaBH_4$ calcined at 800^0C/hr

Table 4.4: Infrared characteristic bands observed in as-prepared ZrO_2 nanopowders and nanopowders calcined at 800^0C/hr.

Band Position (cm^{-1}) Reaction with $NaBH_4$		**Remarks**
As-prepared	Heat-treated at 800 °C	
3414		O-H stretching in $ZrO(OH)_2.xH_2O$ or adsorbed water
2976		
2929		
1640		O-H bending in H_2O
1560		O-H bending in H_2O
1385	1395	O-H bending in $ZrO(OH)_2$
1340		O-H bending in $ZrO(OH)_2$
1088		Zr-O vibration
1050	1005	Zr-O vibration
880		Zr-O vibration

For ZrO_2 powders synthesized by NH_4OH:

Infra-Red spectra in the range of 400 – 4000 cm^{-1} for as-prepared ZrO_2 powders and nanopowders calcined at 700^0C/hr synthesized using NH_4OH was shown in Fig. 4.13 and Fig 4.14 respectively. Individual bands of the Zr-O group vibrations exist in both $ZrO_2.xH_2O$ and ZrO_2. Also O-H bending and stretching vibrations exist in $ZrO_2.xH_2O$ and H_2O molecule. The OH group is distinguished easily in H_2O molecule by its bending vibration which appears in a single band at ~1625 cm^{-1} that confirms the presence of water in the as-prepared powder. Another O-H bending vibrations in the hydroxyl group in the $ZrO_2.xH_2O$ molecule appears at ~ 1350cm^{-1} and one asymmetric O-H stretching band occurs in H_2O around 3414 cm^{-1}. From the IR spectra, the as-prepared powders reveal that the ZrO_2 nano powders have significant amount of surface-adsorbed H_2O. The infrared characteristics bands observed in the as-prepared ZrO_2 nanopowders and those calcined at 700^0C/hr prepared through NH_4OH are given in Table 4.5.

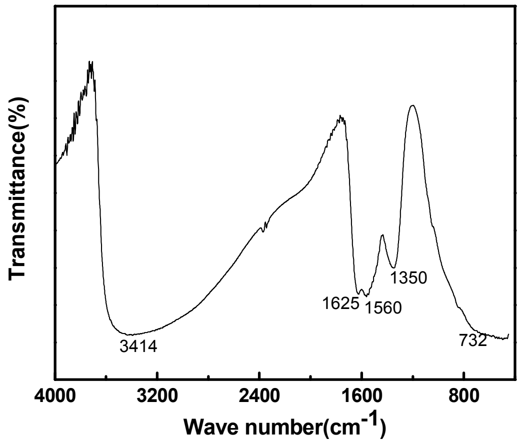


Fig. 4.13: IR spectra of as-prepared ZrO_2 powder synthesized from NH_4OH

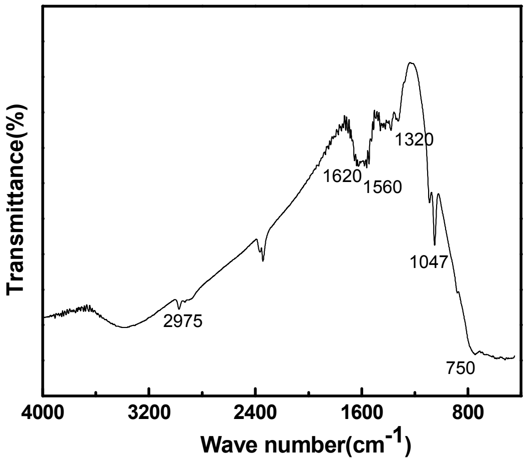


Fig. 4.14: IR spectra of ZrO_2 powder synthesized from NH_4OH calcined at 700^0C/hr

Table 4.5: Infrared characteristic bands observed in as-prepared ZrO_2 nanopowders and nanopowders calcined at 700^0C/hr.

Band Position (cm^{-1}) Reaction with NH_4OH		**Remarks**
As-prepared	Heat-treated at 700 °C	
3414		O-H stretching
	2975	O-H stretching
1625	1620	O-H bending in H_2O
1560	1560	O-H bending in H_2O
1350	1320	O-H bending in $ZrO(OH)_2$
	1047	O-H bending
732	750	Zr-O vibration

CONCLUSIONS:

The significant findings of this work are:

1. Using $NaBH_4$ as a reducing agent we have been able to obtain a tetragonal zirconia successfully upto 900^0C.
2. It was also noticed that concentration of $NaBH_4$ played an important role in the tetragonal phase formation from amorphous powder. An increase in concentration of $NaBH_4$ from 0.5 M to 5M we have been able to shift the onset of crystallization peak of tetragonal Zirconia from 716^0C to 800^0C.
3. From the XRD results it has been concluded that small crystallite sizes (<25 nm) stabilizes tetragonal Zirconia upto moderate temperature.
4. From the TEM, the particle size was in the range of <20 nm
5. On comparing the two synthesis routes we can conclude that $NaBH_4$ is more efficient in shifting the onset of tetragonal phase of Zirconia. The DSC-TG result also supported the XRD analysis and showed the early crystallization of NH_4OH based powder at around 462^0C.
6. In the process the reducing agent $NaBH_4$ which works by controlling the particle size, and also the factor pH which was maintained constant throughout the experiment which contributed in the retention of tetragonal zirconia upto 900^0C.

FUTURE WORK

1. We can prepare thin flims from the bulk powders and measure its dielectric constant.
2. More work needs to be done in the area of application of zirconia as a high –K dielelctric material.
3. In addition to keeping the pH constant we can also control another processing parameter like temperature and see the effect on the phase evolution of zirconia.
4. We can study the effect of addition of surfactant which can help in preventing agglomeration.

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