

EFFECT OF NICKEL CONCENTRATION ON STABILIZATION OF TETRAGONAL ZIRCONIA

*A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF*

Bachelor of Technology

in

Ceramic Engineering

By

Arpit Agrawal

Department of Ceramic Engineering

National Institute of technology

Rourkela-769008

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Under the guidance of

Prof. Bibhuti B. Nayak

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CERTIFICATE

This is to certify that the thesis entitled, “**Effect of nickel concentration on stabilization of tetragonal zirconia**” submitted by Mr **Arpit Agrawal** 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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ARPIT AGRAWAL

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ABSTRACT

The present work deals with effect of particle size, concentration of nickel, and calcination temperature on the enhancement of tetragonal zirconia nanopowders. Nanocrystalline tetragonal zirconia is commercially very significant material which finds extensive use as an anode material in SOFC, as a catalyst oxygen sensor and structural material.

In the present project work, nanocrystalline zirconia powders were prepared by co-precipitation technique. This technique is very helpful for the promotion of the stabilization of t-phase of ZrO₂ at nano level at moderate temperature which is one of the primary objectives of this project. Here the main objective is to stabilize the t-ZrO₂ through precipitation route using NH₄OH. The concentration of nickel-salt plays an important role for the enhancement of stabilized tetragonal phase at moderate temperature. From XRD results it has been concluded that stabilization of t-ZrO₂ was better for 20 mol% nickel-salt concentration as compared with 40 mol% Ni-salt at the same temperature.

CHAPTER 1

GENERAL INTRODUCTION

1. Introduction

Zirconia is an important ceramic material, finds vast application as structural ceramic due to its special characteristics as follows:

- High thermal stability
- High bending strength
- High fracture toughness
- High ionic conductivity

2. Phase transformation of Zirconia

Zirconia in pure form, exhibits three well-defined polymorphs. At room temperature, zirconia has a monoclinic crystal structure, the monoclinic structure to a tetragonal form above 1170 °C and to a cubic fluorite structure above 2370 °C. The monoclinic/tetragonal transformation in zirconia is thermodynamically reversible but associated with large volume change (3 to 5%), i.e. contraction on heating and expansion on cooling. The cubic phase exists up to the melting point of 2680 °C. However, the addition of certain aliovalent oxides can stabilise the cubic fluorite structure of zirconia from room temperature to its melting temperature.

Structure of zirconia

At high temperature zirconia shows cubic fluorite structure (CaF_2). The fluorite structure is adopted tetravalent by a number of oxides of the general formula MO_2 , where M is large cation, e.g. Zr^{+4} , Ce^{+4} etc. The unit cell of the fluorite-type oxide has the so called M_4O_8 structure. This structure is schematically shown in Figure 1.1.

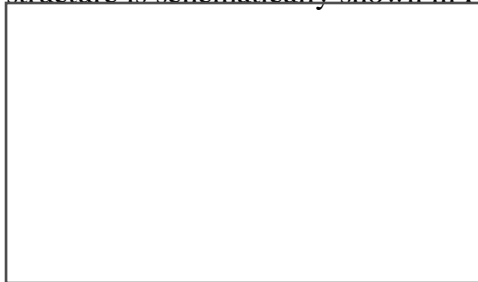


Fig.1.1 crystal structure of zirconia

In this Fluorite structure, each metal ion is surrounded by 4 metal ions, forming a tetrahedral arrangement to form the fluorite structure in MO_2 , the limiting (minimum) ionic radius ratio (the ratio of metal ion radius to oxygen ion radius) is 0.732. Under the normal conditions of temperature and pressure, certain MO_2 oxides do not have In this fluorite structure, each metal ion is surrounded by 8 oxygen ions, forming a body-centered cubic structure, and each oxygen ion is the fluorite structure because the ionic radius ratio condition is not satisfied; one ex is ZrO_2 . At room temperature, ZrO_2 has a monoclinic crystal structure. The monoclinic structure changes to tetragonal form above 1170 °C. However the addition of certain aliovalent oxides stabilize the fluorite structure of ZrO_2 from room temperature to its melting point of 2680 °C. The fluorite structure of ZrO_2 is stabilized by direct substitution of divalent or trivalent cations of appropriate

size for the host lattice cation Zr^{+4} . In this case, lattice defects are created to preserve the electroneutrality condition in the solid solution. The probable models for structural defects are in such cases are:

1. An oxygen ion vacancy model with all the metal ions being fixed at their lattice points.
2. A cation interstitial model with all the oxygen ions being fixed at their lattice sites.

It is well established that the oxygen ion vacancy model applies to stabilize ZrO_2 . The presence of a high oxygen vacancy concentration in stabilized ZrO_2 gives rise to a high oxygen ion mobility, resulting in high oxygen ion conductivity. Oxygen ion conduction takes place in stabilized ZrO_2 by movement of oxygen ion via vacancies.

3. Stabilization of zirconia

The common stabilizing agents used for the stabilization of zirconia are CaO , Y_2O_3 , MgO , Sc_2O_3 and certain rare earth oxides. These oxides exhibit a relatively high solubility in ZrO_2 and are able to form various solid solutions with ZrO_2 , including cubic fluorite solid solutions which are stable over a wide range of temperature and composition.

Fig 1.2 phase diagram of ZrO₂-CaO system

Figure 1.2 shows the equilibrium phase diagram for ZrO₂-CaO system (where M_{ss}, T_{ss} and C_{ss} indicate monoclinic, tetragonal and cubic solid solution resp.). The system has a eutectoid at about 17 mol% of calcium oxide in the composition range CaO-CaZrO₃ from 6-17 mol% of calcium oxide, the material consists of tetragonal solid solution and monoclinic solid solution phases above 1140^o C. Slow cooling from 1140^oC to 1000^oC results in the tetragonal solid solution phase and CaZr₄O₉. Further cooling below 1000^oC causes the martensitic transformation of tetragonal solid solution to monoclinic solid solution. The cubic phase is thermodynamically unstable at low temperatures. The eutectoid decomposition of cubic solid solution occurs at 1140^oC.

Fig 1.3 phase diagram of ZrO₂-Y₂O₃

Figure 1.3 shows the phase diagram of ZrO₂-Y₂O₃ system. It is clear from the phase diagram that the addition of Y₂O₃ to ZrO₂ reduces the temperature of tetragonal to monoclinic transformation and it decreases with the increase in Y₂O₃ content (in the composition range 0-2.5

mol% of Y_2O_3 . In this composition range, the tetragonal solid solution is transformable i.e. the tetragonal phase will transform on cooling to monoclinic phase. At higher Y_2O_3 content, a mixture of non-transformable tetragonal and cubic solid solution exists. Further increase in Y_2O_3 content results in a homogeneous cubic solid solution. The minimum Y_2O_3 amount required to fully stabilize the cubic phase of ZrO_2 is about 8-10 mol% at 1000°C.

1.4 Role of NiO for the stabilization of zirconia

Like other dopants such as Y_2O_3 , Sc_2O_3 , CaO , MgO , nickel oxide is a very good dopant for stabilization of zirconia. The amount of dopant concentration and particle size of dopants greatly affects the physical properties of zirconia. A chemical reaction occurs between NiO and ZrO_2 , the ionic radius of Ni^{+2} being smaller compared to the size ZrO_2 . This gives rise to a solid-solution of nickel oxide and zirconia. The particle size of nickel oxide grains have a great effect on the stabilization of tetragonal phase of zirconia. The formation of the tetragonal solid-solution of $NiO-ZrO_2$ is believed to be due to the smallness of grains, hence, the enhanced surface reactivity and diffusion of the atoms at the surface. In general, the stabilization of tetragonal/cubic phase of zirconia has been found to be dependant on many parameters such as ionic size of dopant, valency, electronegativity etc. However the extent of tetragonal solid solution is dependant on the dopant concentration.

1.5 Application of NiO- ZrO_2

- For the preparation of anode material in SOFC.
- As a catalyst in partial oxidation of methane into higher hydrocarbons.
- As a catalyst for steam reforming of methane and methanol.
- As a solid electrolyte in oxygen sensor.

CHAPTER 2

LITERATURE REVIEW

2.1 Effect of dopant concentration, crystallite size and duration of calcination for the stabilization of tetragonal zirconia

A. Chandra Bose, R. Ramamoorthy, S. Ramasamy, "Formability of metastable tetragonal solid solution in nanocrystalline NiO-ZrO₂ powders", Materials Letters 44, 203-207 (2000)

It is found that the presence of the tetragonal phase is either due to the dopant effect or the grain size effect. The formation of the tetragonal solid solution of NiO-ZrO₂ is believed to be due to the smallness of the grains, hence, the enhanced surface reactivity and diffusion of the atoms at the surfaces. In general, stabilization of the tetragonal/cubic phase of ZrO₂ has been found to be dependent on many parameters such as ionic size of the dopant, valence, electronegativity, etc. However, the extent of the tetragonal solid solution is dependent on the dopant concentration (here the NiO). The maximum volume percentage of the tetragonal phase is observed for 20 vol% NiO at an annealing temperature of 800°C. The reasons for the reduced fraction of the tetragonal phase in 30 mol% NiO-ZrO₂ may be the following: The increased concentration of the dopant NiO helps nucleation of crystallites and enhances grain growth. The higher the grain size, the lesser the surface area and hence, reduced reactivity of the surface atoms. Thus, the diffusion of Ni-O atoms from the nearby NiO clusters into the lattice of ZrO₂ crystallites in touch with them will be reduced. The formability of the metastable tetragonal solid solution of NiO-ZrO₂ has been observed by NiO doping and reduction in grain size.

Songali Li, Ruisong Guo, Jinyou Li, Yuru Chen, Wenxi Liu., Synthesis of NiO-ZrO₂ powders for solid oxide fuel cells. Ceramics international, 29, 883-886 (2003)

Very fine nanosized NiO-ZrO₂ was synthesized by co-precipitation method. cubic NiO and cubic ZrO₂ was obtained after calcination at 600°C. powders calcined at different temperatures showed different particle distribution. when NH₃.H₂O was used as co-precipitation agent, a great deal of Ni⁺² loss led to the deviation from initial composition. when NH₃.H₂O-NH₄HCO₃ was used as co-precipitation agent, PH value can be better controlled and yield had been raised to some extent.

Hiroki Kondo, Tohru Sekino, Takafumi Kusunose, Tada Chika Nakayama, Yo Yamamoto, Koichi Niihara., Phase Stability And Electrical Property Of NiO-doped Yttria Stabilized Zirconia, Materials Letters, 57, 1624-1628 (2003).

The effect of NiO solid solution on the stability of YSZ and time dependent ionic conductivity were investigated. It was found that Raman spectroscopy analyses that NiO-doped YSZ showed only the cubic phase, whereas monolith has a small amount of tetragonal phase aside from the cubic phase. YSZ monolith showed time dependent decline in ionic conductivity at 1000°C.

Satyajit Shukla, Sudipta Seal, Rasmi Vij, Bandyopadhyay, Zia Rahman., Effect Of Nanocrystallite Morphology On The Metastable Tetragonal Phase Stabilization In Zirconia, Nano Letters, Vol. 2, No. 9, 989-993 (2002).

Nanosized (20-25 nm) and submicron sized (500-600 nm) monodispersed, spherical

ZrO₂ particles are successfully synthesized using sol-gel technique. The tendency of ZrO₂ nanocrystallites (45 nm) to form a hard aggregate observed to be responsible for higher temperature metastable tetragonal phase stabilization at room temperature, within the submicron-sized ZrO₂ particles.

R. Srinivasan, L. Rice, B. H. Davis, Critical particle size and phase Transformation in Zirconia: Transmission Electron Microscopy and X-ray Diffraction Studies, American ceramic society, 73, 3528 (1990)

A study was undertaken to examine the crystallite size effect on the low-temperature transformation of tetragonal zirconia. Zirconia was prepared by precipitation from a solution of zirconium tetrachloride by adding ammonium hydroxide to produce a pH of 2.95. Portions of the sample, after drying, were calcined at 500°C for various time intervals. Phase transformation was followed by X-ray diffraction; the data shows that the tetragonal phase was initially formed and it was transformed to the monoclinic phase at longer periods of calcinations. It was observed that TEM particle size and XRD crystallite size that the transformation does not appear to be due to a critical particle size effect.

N. L. Wu and T. F. Wu, Enhanced phase stability for Tetragonal Zirconia in precipitation synthesis, J. Am. Ceramic Soc., 83, 3225 (2000)

Tetragonal ZrO₂ nanocrystallites with or without Yttria (3 mol%) doping have been synthesized via a precipitation process in which the hydrous oxide precipitate reacts with hexamethyldisilazane vapour before calcinations. The nanocrystallites are formed and retain a tetragonal structure for hours after calcinations at temperatures of 300^o-1100^oC. The enhanced structural metastability has been attributed to the combined effect of suppressed grain growth and reduced surface energy.

2.2 Summary of Literature Survey

TITLE	RESULT	REFERENCE
Formability of metastable tetragonal solid solution in nanocrystalline NiO-ZrO ₂ powders.	The concentration of dopant NiO influences the grain size. The variation in grain size seems to influence the formation of metastable tetragonal state of NiO-ZrO ₂ . 20 mol% NiO-ZrO ₂ gives cubic fluorite stabilized zirconia below 6000C.	Bose et. al. Materials Letters 44, 203-207 (2000)
Synthesis of NiO-ZrO ₂ powders for solid oxide fuel cells.	Very fine powders can be synthesized. Cubic NiO and cubic ZrO ₂ obtained after calcination at 6000c.	Li et. al. Ceramics international, 29, 883-886 (2003).
Phase Stability And Electrical Property Of NiO-doped Yttria Stabilized Zirconia.	Addition of nickel enhanced the ionic conductivity of zirconia.	Kondo et. al. Materials Letters, 57, 1624-1628 (2003).
Effect Of Nanocrystallite Morphology On The Metastable Tetragonal Phase Stabilization In Zirconia.	the tendency of ZrO ₂ nanocrystallites (45 nm) to form hard aggregate observed to be responsible for higher temperature metastable tetragonal phase, stabilization at room temperature, within the submicron sized ZrO ₂	Shukla et. al. Nano Letters, Vol. 2, No. 9, 989-993, 2002.

	particles.	
Critical particle size and phase Transformation in Zirconia: Transmission Electron Microscopy and X-ray Diffraction Studies	t-phase would be stabilized in particle of diameter 30nm or small.	Srinivasan et. al. American ceramic society 73,3528 (1990)
Enhanced phase stability for tetragonal Zirconia in precipitation Synthesis	Monoclinic phase exists < 4000C Size of ZrO ₂ crystallite increases as the calcinations temp. increases from 8nm at 4000C to 25nm at 9000C .	Wu et. al. Journal of American ceramic society 83,3225-27(2000)

The important facts can be summarized from literature review as follows:

1. There are different techniques for the stabilization of ZrO₂.
2. Different polymorphs of ZrO₂ are dependent on crystallite size and calcination temperature.
3. Addition of nickel into zirconia leads to suppression of monoclinic phase and enhancement of tetragonal phase.
4. An optimum amount of nickel concentration for development of tetragonal phase was found to be around 20mol% NiO.
5. Stabilization of t-phase most likely due to low surface energy of the t-phase relative to m-phase.
6. Above a certain concentration of nickel there is decrease in tetragonal phase .this is due to lattice strains.
7. Stabilization of tetragonal phase in most cases is upto 500⁰C and monoclinic phase is upto 1000⁰C.

3. Objectives

Till today so many works have been done to obtain the high temperature cubic phase and tetragonal phases in a thermodynamically stable at low temperature using different synthesis techniques like sonochemical, hydrothermal, chemical precipitation and sol-gel etc. My project emphasis on

- 1) Synthesis and stabilization of tetragonal zirconia by varying the Ni-salt concentration.
- 2) Analyse thermal, structural, microstructural and IR results.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Synthesis

Nano sized particles of Ni stabilized zirconia particles was prepared through co-precipitation technique using NH_4OH solvent. An aqueous solution of 1M (where M is the molarity) concentration of Zr-salt ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) were prepared from high purity Zr-salt which is highly acidic in nature having a $\text{pH}=0.3$ where as the pH of NH_4OH found to be 12.83 which is highly basic in nature. NH_4OH solution was added dropwise to a beaker containing 1 M (1-x) mole % Zr-salt and 1 M x mole % Ni-salt ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) [where $x = 0, 20$ and 40] solution with constant stirring by a magnetic stirrer. A gel was formed and excess addition of NH_4OH solution leads to precipitation was allowed to settled out. The precipitate was washed with hot water for several times to remove chlorine from solution. The precipitate was dried in an oven at 80°C for 24 hours. The dried sample so obtained was crushed and grinded to obtain very fine powder. The fine powder was calcined at 700°C , 800°C and 900°C for 1 hour.

The precipitate was dried in an oven at 80°C for 24 hour followed by grinding and crushing so as to get fine powder. The fine powder was calcined at 700°C , 800°C and 900°C for 1 hour. The schematic flowchart for the preparation and charecterisation of nano sized zirconia powder is as shown below.

Schematic flow chart for synthesis of Ni-doped ZrO_2

3.2 General characterization

3.2.1 Thermal analysis:

Thermal decomposition of $ZrO(OH)_2$ gel to an amorphous ZrO_2 powder followed by its reconstructive nucleation of t- ZrO_2 nanoparticles were studied using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at 100C/min in N_2 atmosphere in a thermal analyser (Model Netzsch, STA 449C). Alpha alumina was used as reference material.

3.2.2 X-ray diffraction

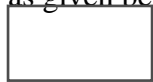
Phase analysis was studied using the room temperature powder X-ray diffraction (Model) with filtered 0.154056 nm Cu K(radiation. Samples are scanned in a continuous mode from 20° - 80° with a scanning rate of 0.04 (degree)/1sec.

3.2.3 Scanning Electron Microscope

Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan). For preparation of SEM sample, the powder is 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 is deposited on to polished brass plate. This brass plate was used for microscopy.

3.2.4 Particle size measurement

Size of the particles is usually obtained with the help of scanning electron microscopy (SEM). The size corresponds to the mean value of the crystalline domain size of the particles is determined from the X-ray line broadening using Debye-Scherrer formula with correction factor as given below,



Where $(= (\delta_{\text{sample}}^2 - \delta_{\text{standard}}^2$
(= the angular line width of half maximum intensity
d = crystallite size,
(= X-ray wavelength used
(= the Bragg's angle in degree
 δ_{standard} = the angular line width of half maximum intensity for polycrystalline SiO_2 material

CHAPTER 4

RESULT AND DISCUSSION

This chapter describes the structural, thermal, and Infra-Red analysis of ZrO_2 nanoparticles prepared through co precipitation technique using NH_4OH .

4.1 Thermal Analysis

The thermal behavior of the nanocrystalline Ni doped ZrO_2 powder is studied upto 1000°C using DSC/TG analysis. It is clear from the Fig 4.1 that it exhibits an endothermic peak at a temperature of 116 °C due to evolution of water absorbed on the as-prepared powder. With

increasing temperature, it shows a very sharp exothermic peak at 446⁰C related to fast crystallization into metastable tetragonal Zirconia. To make certain of the structure of the as-synthesized powder, the thermogravimetric analysis (TGA) is conducted. The TGA analysis shows that the weight loss is approximately 31%. The humps in the range of 300-400⁰C indicate the decomposition of Zirconium hydroxide ZrO(OH)₂ to ZrO₂.

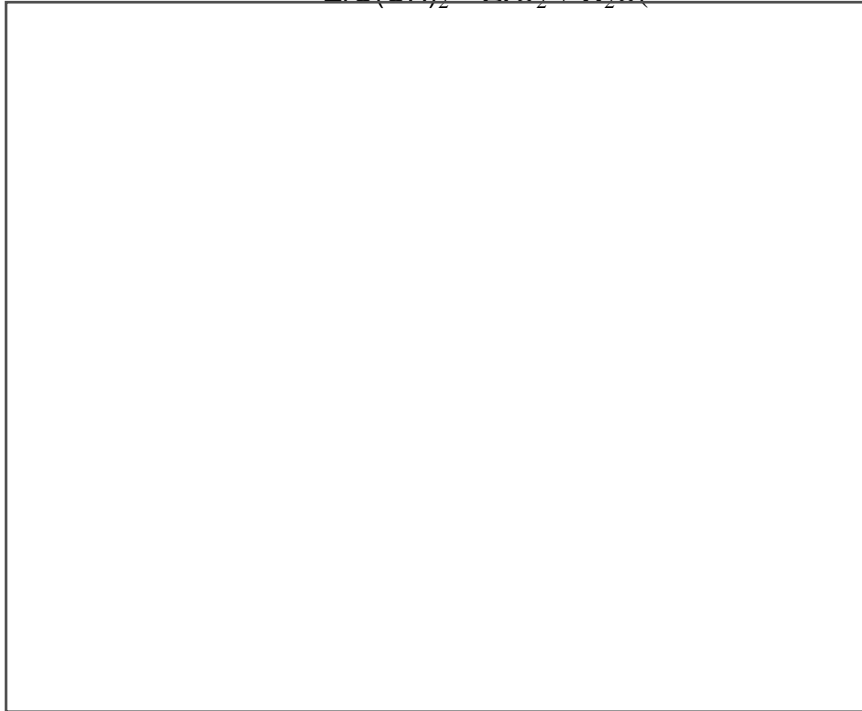
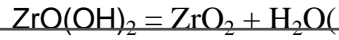


Fig 4.1 DSC-TG of pure ZrO₂

From fig .4.2 it is clear that the DSC-TG graph has two endo thermic peaks at temperature 123⁰C & 329⁰C. It may be due to the evaporation of water absorbed by as prepared 40 mol% Ni ZrO₂. As compared to pure zirconia powder, Ni doped ZrO₂ shows two endothermic peaks. Further increase in temperature gives a sharp exothermic peak at a temperature 630⁰C related to fast crystallization into metastable tetragonal Zirconia. To make certain of the structure of the as-synthesized powder, the thermogravimetric analysis (TGA) is conducted.

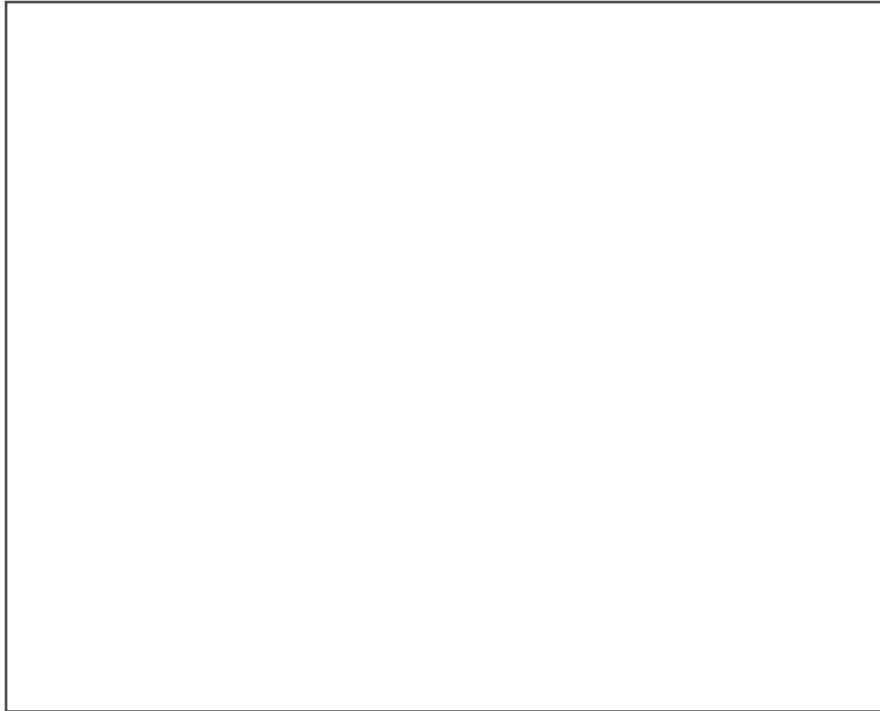


Fig 4.2 DSC-TG of 40 mol% Ni ZrO₂

4.2 Structural analysis (XRD analysis)

By co-precipitation technique the 1M ZrO₂, 0.2M NiO-0.8ZrO₂ and 0.4NiO-0.6ZrO₂ was reacted with NH₄OH by maintaining a final pH around 10. Fig.4. 1 shows the XRD spectra of as-prepared ZrO₂ powder, 20 mol%, and 40 mol% Ni doped ZrO₂ nanocrystalline powder calcined at 700°C. The crystallite NiO peaks are observed at $2\theta = 36.83, 42.88, 62.52$ and indicate its presence as a second phase. From XRD spectra it is quite clear that in pure zirconia powder the monoclinic phase is dominant. With 20 mol% addition of nickel, the monoclinic phase is suppressed and the tetragonal phase is enhanced. Development of NiO along with t-ZrO₂ was observed for 40 mole % Ni doped ZrO₂ powders. The crystallite size of pure zirconia, 20 mol% and 40 mol% nickel doped ZrO₂ were calculated using Scherrer's formula and found to be 46.3nm, 27.8nm and 139.5nm respectively.



Fig. 4.1: X-ray diffraction patterns of different mole % Ni doped ZrO_2 heat-treated at $700^\circ C$

Figure 4.2 shows the XRD spectra of as-prepared ZrO_2 powder, 20 mol% and 40 mol% Ni doped ZrO_2 nanocrystalline powder calcined at $800^\circ C$. From XRD spectra it is quite clear that in pure zirconia powder the presence of monoclinic phase is dominant. With 20 mol% addition of nickel suppress the monoclinic phase and enhanced the tetragonal phase. Further addition of Ni i.e. 40 mol% leads to development of NiO along with t- ZrO_2 . The crystallite size of pure zirconia, 20 mol% and 40 mol% nickel doped ZrO_2 were calculated using Scherrer's formula and found to be 24.4 nm, 27.8 nm and 22 nm respectively.



Fig. 4.2: X-ray diffraction patterns of different mole % Ni doped ZrO₂ heat-treated at 800°C

Figure 4.3 shows the XRD spectra of as-prepared ZrO₂ powder, 20 mol% and 40 mol% Ni doped ZrO₂ nanocrystalline powder calcined at 900°C. By analyzing the XRD pattern it was found that in case of pure zirconia powder the major phase is monoclinic with minor amount of tetragonal phase (~99% m and ~1% t). At 20 mol% Ni addition the monoclinic phase suppressed to 40 vol% and tetragonal phase developed to ~60 vol % with presence of minor amount of NiO phase (~5 vol%). Further addition of nickel concentration leads decrease in tetragonal phase and increase in monoclinic as well increase of NiO phase. This may be due the following reasons:

- 1) The increased concentration of dopant NiO helps nucleation of crystallites and enhances grain growth. The size is found to be larger in 40 mol% compared to other composition of powders.
- 2) Higher grain size is inversely proportional to surface area so reduced reactivity.
- 3) Crystallite size of pure zirconia, 20 mol% and 40 mol% nickel doped ZrO₂ were calculated using Scherrer's formula and found to be 37.7 nm, 37.9 nm and 59.6 nm respectively.

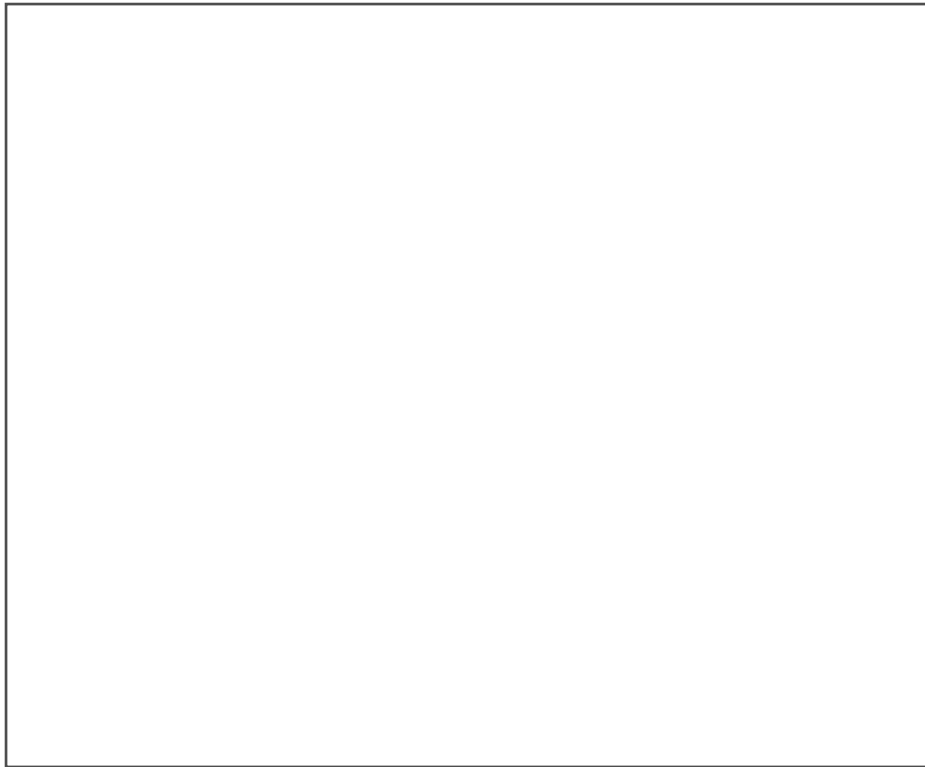


Fig. 4.3: X-ray diffraction patterns of different mole % Ni doped ZrO₂ heat-treated at 900°C

STANDARD JCPDS FILE

Table 4.1: MONOCLINIC PHASE OF ZrO₂

2θ	INTERPLANAR SPACING	INTENSITY	INDICES OF PLANE(hkl)
28.219	3.1598	999	-111
31.503	2.8375	670	-111
34.179	2.6213	202	002
34.467	2.6000	125	020
35.336	2.5380	144	200
40.778	2.2110	129	211
49.327	1.8459	171	022
50.192	1.8161	208	220
51.275	1.8012	118	122
54.127	1.7803	51	221
54.127	1.6930	112	202

JCPDS FILE NO:PDF#830944

2θ	INTERPLANAR SPACING	INTENSITY	INDICES OF PLANE(hkl)
30.509	2.9300	100	111
35.193	2.5500	25	200
50.686	1.8010	50	220

Table 4.2: TETRAGONAL PHASE OF ZrO₂

JCPDS FILE NAME: PDF # 270997

Table 4.3: CUBIC PHASE OF Ni

JCPDS FILE NAME: PDF # 040850

2 θ	INTERPLANAR SPACING	INTENSITY	INDICES OF PLANE (hkl)
44.505	2.03040	100	111
51.844	1.7620	42	200

Table 4.4: CUBIC PHASE OF NiO

JCPDS FILE NAME: PDF #780643

2 θ	INTERPLANAR SPACING	INTENSITY	INDICES OF PLANE (hkl)
37.265	2.4110	67.5	111
43.298	2.0880	100	200

Here we may conclude that at higher concentration of Ni in Ni-ZrO₂ composite which is calcined at high temperature, t-phase of ZrO₂ is completely stabilized and it also shows the effect of NiO prominently. So, this is the perfect condition of the sample which is liable for practical application.

4.3 IR spectroscopy

Infra-Red spectra in the range of 500 – 4000 cm^{-1} for as-prepared ZrO_2 as well as Ni doped ZrO_2 powders synthesized using NH_4OH was studied. Fig. 4.4 and Fig. 4.5 show the IR result of as-prepared ZrO_2 and calcined (800 $^\circ\text{C}$) ZrO_2 respectively. Fig. 4.6 and Fig. 4.7 show the IR result of as-prepared 20 mol % Ni doped ZrO_2 and calcined (800 $^\circ\text{C}$) 20 mol % Ni doped ZrO_2 respectively. From the IR spectra, the as-prepared powders reveal that the ZrO_2 nano powders have significant amount of surface-adsorbed H_2O molecules. As-prepared ZrO_2 as well as doped ZrO_2 calcined at high temperature gives Zr-O vibration as observed from IR spectra. The infrared characteristics bands observed in all the samples prepared through NH_4OH are given in Table 4.5 and Table 4.6.

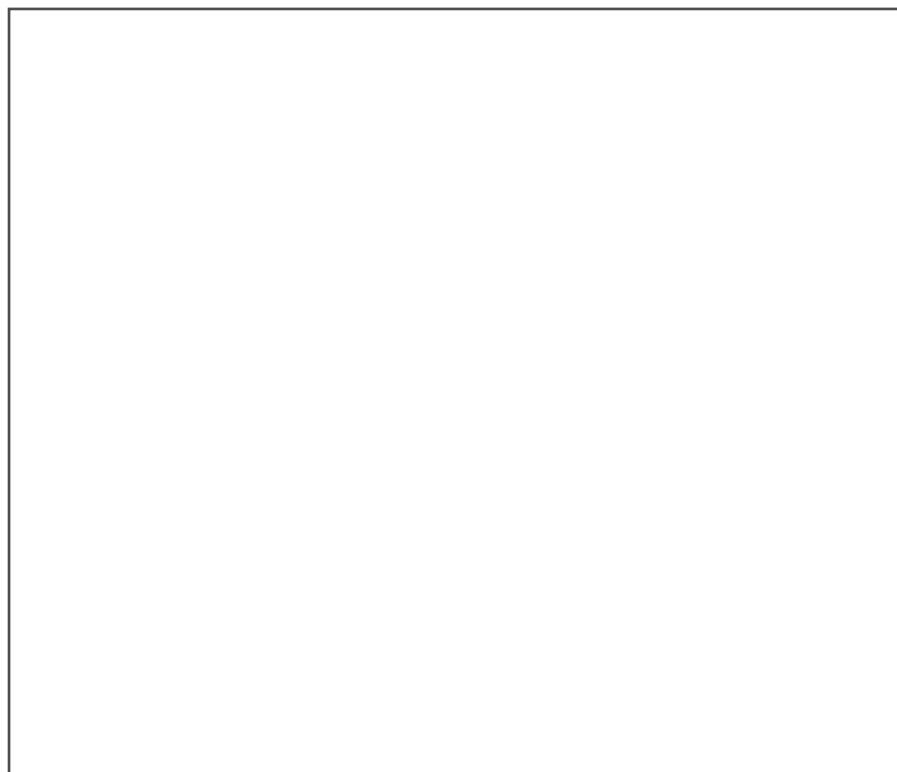


Fig. 4.4: IR spectra of as-prepared ZrO_2

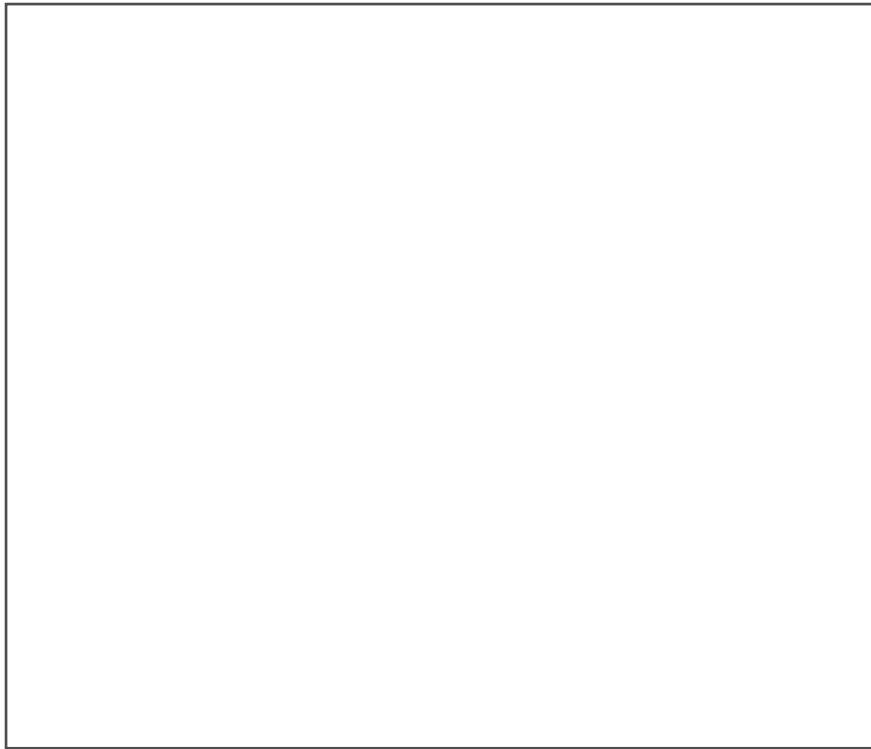


Fig. 4.5: IR spectra of calcined (800 °C) ZrO₂

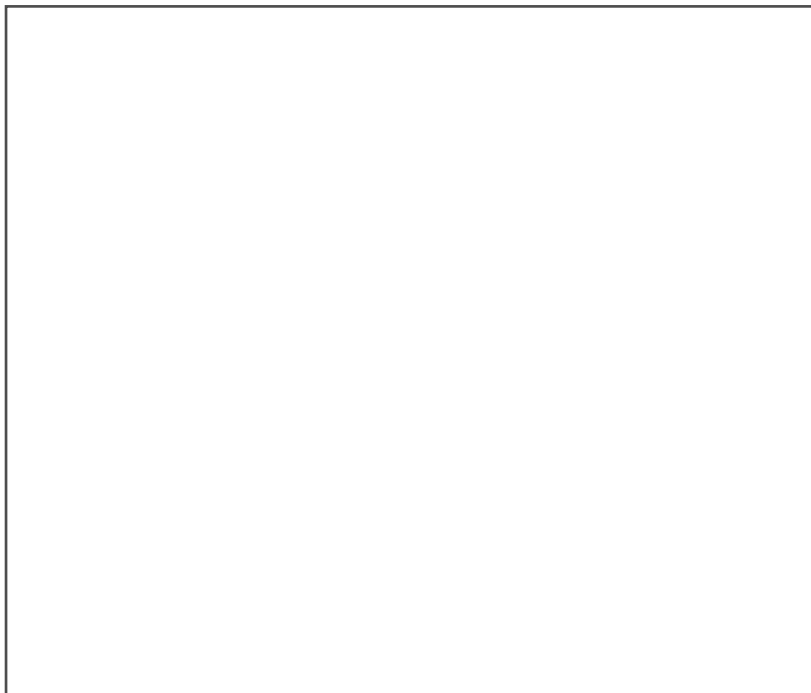


Fig. 4.6: IR spectra of as-prepared 20 mol % Ni doped ZrO₂

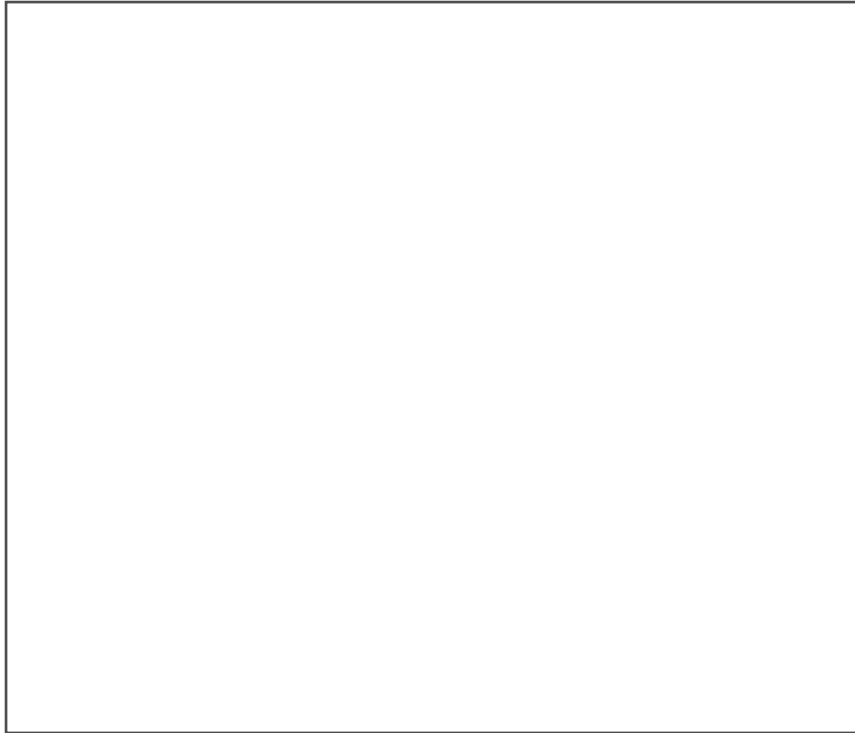


Fig. 4.7: IR spectra of calcined (800 °C) 20 mol % Ni doped ZrO₂

Table 4.5: PURE ZrO₂

AS PREPARED	CALCINED AT 8000C	REMARKS
3401	3446	O-H stretching
2360		O-H vibration
1623		O-H bending
1568		O-H vibration
1340		O-H vibration
740	744	Zr-O vibration
	578	Zr-O vibration
	500	Zr-O vibration

Table 4.6: 20 mole % Ni doped ZrO₂

AS PREPARED	CALCINED AT 8000C	REMARKS
3394		O-H stretching
2366		O-H vibration
1623		O-H bending
1560		O-H vibration
1362		O-H vibration
740	680	Zr-O vibration

CONCLUSIONS

The present work deals with the synthesis and characterisation of nickel doped zirconia. Here, the nanopowders were synthesized by co-precipitation method using NH₄OH. The significance of this work are:

- 1) Stabilization of metastable t- ZrO₂ is observed at 20 mol% of nickel salt at 800°C
- 2) From XRD results it has been concluded that small crystallites (27.8 nm) stabilizes metastable t-ZrO₂ at intermediate temperature range.
- 3) Above a certain concentration of nickel salt there is decrease in tetragonal phase. This is due to presence of lattice strain.

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1M NiCl₂.6H₂O

Added dropwise

Precipitation pH=10

gelation

1 M ZrOCl₂.H₂O

NH₄OH Soln

Characterization (XRD, DSC-TG, IR spectroscopy)

Dried in an oven at 80°C for 24 h

Washed with hot water

Crushing and grinding

Calcined at 700°C, 800°C and 900°C for 1 h