

# Nickel Stabilized Zirconia for SOFCs: Synthesis and Characterization

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**Abstract** Nanocrystalline tetragonal zirconia is commercially very significant material which finds extensive use as an anode material in SOFCs, as a catalyst oxygen sensor and structural material. Nanocrystalline zirconia powders for high performance anode of SOFCs have been synthesized by co-precipitation route. This technique is very helpful for the promotion of the stabilization of tetragonal phase of  $\text{ZrO}_2$  in nano level at moderate temperature. The main objective of this paper is to stabilize the t- $\text{ZrO}_2$  through precipitation route using  $\text{NH}_4\text{OH}$  solution. The processing features and the microstructural characteristics of  $\text{NiO-ZrO}_2$  have been investigated by DSC-TG, XRD, SEM, and IR spectroscopy. The concentration of nickel-salt plays an important role for the enhancement of stabilized tetragonal phase at moderate temperature. From XRD results it was found that the t- $\text{ZrO}_2$  was more stabilized with 20 mol% nickel-salt concentration compared with 40 mol% Ni-salt at the same temperature.

**Keywords** Ni stabilized  $\text{ZrO}_2$ , Synthesis, Co-precipitation Route

## 1. Introduction

Solid oxide fuel cells (SOFCs) are environmentally friendly energy conversion systems to produce electrical energy with minimal environmental impact[1-4]. The efficient operation of SOFC anode is strongly depends on its microstructural parameters such as particle size, composition and spatial distributions of the constituent phases. Most present SOFCs developers use yttria-stabilized zirconia (YSZ) as electrolyte, strontium-doped lanthanum manganite (LSM) as cathode and Ni-YSZ ceramic metallic composite (cermet) as supported anode materials[5-7]. Ni-YSZ cermet is an electronic conductive material formed during the SOFC stack operation by the reduction of NiO-YSZ used at the anode site during cell fabrication process. NiO-YSZ is an insulating material and its complete reduction to Ni-YSZ is necessary to assure good anodic performance. Ni-YSZ cermets have been used as SOFC anodes mainly due to their high electronic conduction, good electrochemical performance in the intermediate temperature range (750–850°C) and high catalytic activity in reform reactions and the comparatively low cost of nickel[7-8]. During the chemical reaction occurs between NiO and  $\text{ZrO}_2$ , the ionic radius of  $\text{Ni}^{+2}$  being relatively small compared to the size of  $\text{ZrO}_2$  and this gives rise to a solid-solution of nickel oxide and zirconia. The particle size of nickel oxide has a great

effect on the stabilization of tetragonal phase of zirconia[9-11]. The formation of the tetragonal solid-solution of  $\text{NiO-ZrO}_2$  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.[12].

The presence of the tetragonal phase is due to the effect of either the dopant concentration or the grain size of the dopant. The formation of the tetragonal solid solution of  $\text{NiO-ZrO}_2$  is believed to be due to the smallness of the grains, hence, the enhanced surface reactivity and diffusion of the atoms at the surfaces[13-14]. In general, stabilization of the tetragonal/cubic phase of  $\text{ZrO}_2$  has been found to be dependent on many parameters such as ionic size of the dopant, valence, and electronegativity[15].

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. In this paper, we are emphasis on the synthesis and stabilization of tetragonal zirconia by varying the Ni-salt concentration. Thermal, structural, microstructure analysis and as well as IR spectroscopy were carried out

## 2. Experimental Procedures

### 2.1. Synthesis

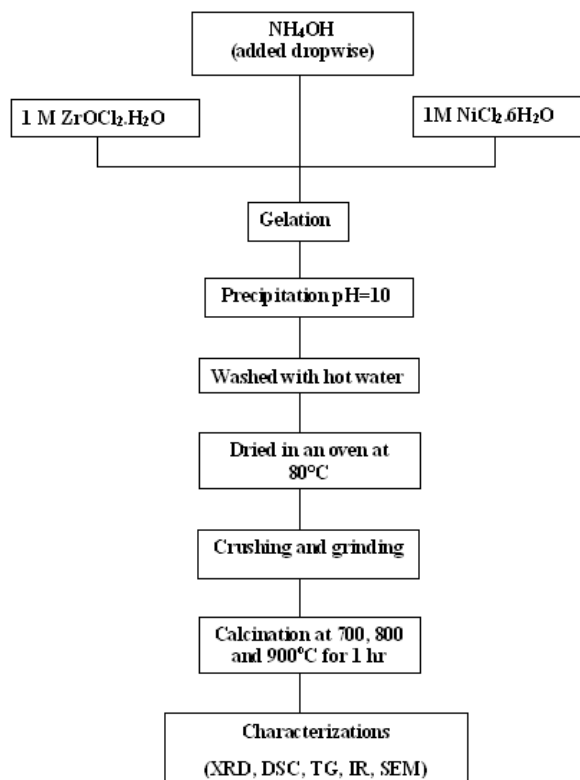
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Nano sized particles of Ni stabilized zirconia particles were prepared through co-precipitation technique using  $\text{NH}_4\text{OH}$  solution. An aqueous solution of 1M (where M is the molarity) concentration of Zr-salt ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) were prepared from high purity Zr-salt which is highly acidic in nature (having a  $\text{pH}=0.3$ ), while the  $\text{pH}$  of  $\text{NH}_4\text{OH}$  solution was found to be 12.83 which is highly basic in nature.  $\text{NH}_4\text{OH}$  solution was added drop wise to a beaker containing 1 M(1-x) mol% Zr-salt and 1Mx mol% 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  $\text{NH}_4\text{OH}$  solution leads to precipitation was allowed to settle out. The precipitate was washed with hot water for several times to remove chlorine from solution. The precipitate was dried at  $80^\circ\text{C}$  for 24 hours. The obtained dried sample was crushed and grinded to obtain very fine powder. The fine powder was calcined at  $700^\circ\text{C}$ ,  $800^\circ\text{C}$  and  $900^\circ\text{C}$  for 1 hour. The whole preparation process is schematically illustrated in Fig. 1.



**Figure 1.** Schematic diagram of the preparation of Ni-doped  $\text{ZrO}_2$  powder

## 2.2. General characterization

Thermal decomposition of  $\text{ZrO}(\text{OH})_2$  gel to an amorphous  $\text{ZrO}_2$  powder followed by its reconstructive nucleation of t- $\text{ZrO}_2$  nanoparticles were studied using thermogravimetric and differential scanning calorimetric (TG-DSC) by heating the sample at  $100^\circ\text{C}/\text{min}$  in  $\text{N}_2$  atmosphere in a thermal analyser (Netzsch, STA 449C). Alpha alumina was used as reference material. Phase analysis was studied using the room temperature powder X-ray diffraction (PW 1830 Diffractometer, Phillips, Netherland) with filtered  $0.154\text{ nm}$

$\text{Cu K}\alpha$  radiation. Samples are scanned in a continuous mode from  $20^\circ$  to  $80^\circ$  with a scanning rate of  $0.04^\circ/\text{sec}$ . Microstructural features were studied using Scanning Electron Microscope (JSM 6480 LV JEOL, Japan).

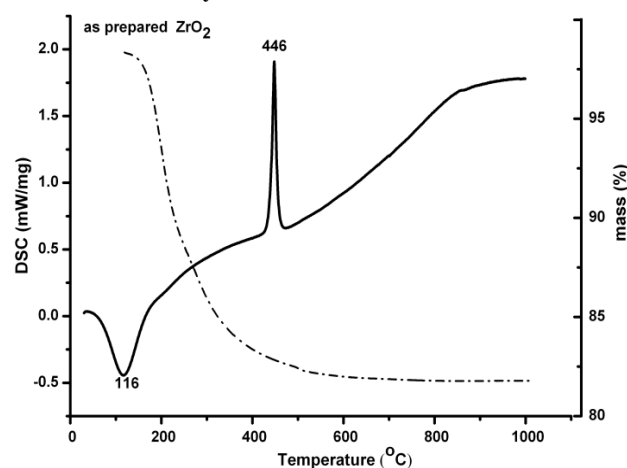
Size of the particles is usually obtained with the help of scanning electron microscopy (SEM). The size corresponds to the mean value of the crystalline domain size of the particles is determined from the X-ray line broadening using Debye-Scherrer formula with correction factor as given below,

$$d \propto \frac{0.9\lambda}{\beta \cos \theta}$$

Where  $\beta$  is the angular line width of half maximum intensity,  $d$  is the crystallite size,  $\lambda$  is the X-ray wavelength used, and  $\theta$  is the Bragg's angle in degree.

## 3. Results and Discussion

### 3.1. Thermal Analysis



**Figure 2.** DSC-TG of pure  $\text{ZrO}_2$

The thermal behavior of the nanocrystalline Ni doped  $\text{ZrO}_2$  powder is studied up to  $1000^\circ\text{C}$  using DSC/TG analysis. It is clearly shown from figure 2 that the as prepared  $\text{ZrO}_2$  powder exhibits an endothermic peak at a temperature of  $116^\circ\text{C}$  due to evolution of water absorbed on the as-prepared powder. With increasing temperature, it shows a very sharp exothermic peak at  $446^\circ\text{C}$  which is related to the 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  $300$ – $400^\circ\text{C}$  indicate the decomposition of Zirconium hydroxide  $\text{ZrO}(\text{OH})_2$  to  $\text{ZrO}_2$ . Figure 3 shows the DSC-TG graph of 40 mol% Ni doped  $\text{ZrO}_2$  powder; it has two endothermic peaks at temperature  $123^\circ\text{C}$  and  $329^\circ\text{C}$ . It may be due to the evaporation of water absorbed by as prepared 40 mol% Ni doped  $\text{ZrO}_2$ . Further increase in temperature shows a sharp exothermic peak at a temperature  $630^\circ\text{C}$  related to the fast crystallization into metastable tetragonal zirconia. To make certain of the

structure of the as-synthesized powder, the thermogravimetric analysis (TGA) is conducted.

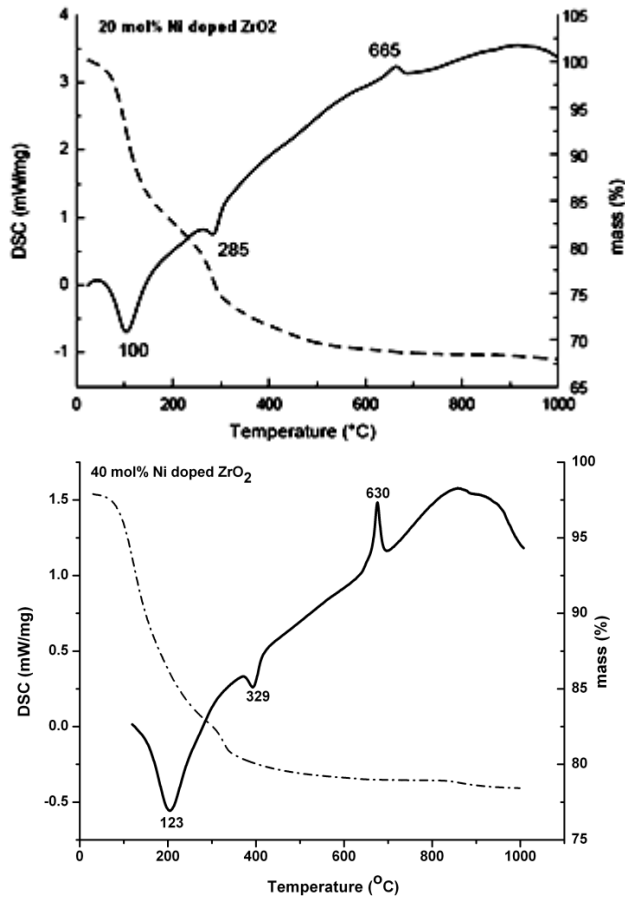


Figure 3. DSC-TG of 20 mol%, and 40 mol% Ni doped ZrO<sub>2</sub>

### 3.2. X-ray Diffraction

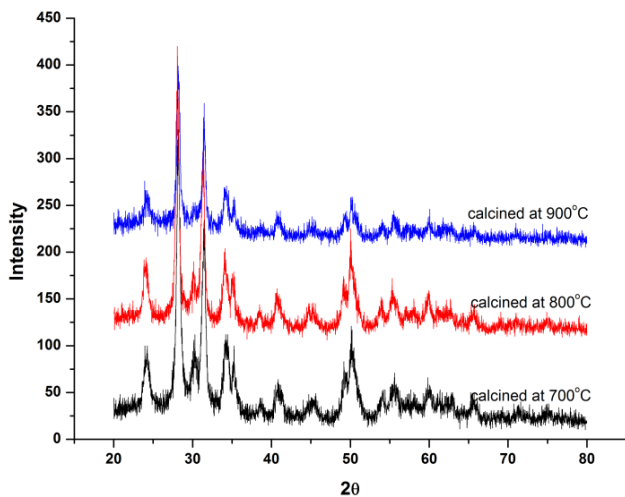


Figure 4. XRD patterns of pure ZrO<sub>2</sub> calcined at different temperatures

By co-precipitation technique, 1M ZrO<sub>2</sub>, 0.2M NiO-0.8ZrO<sub>2</sub> and 0.4M NiO-0.6ZrO<sub>2</sub> were reacted with NH<sub>4</sub>OH by maintaining a final pH to be ~10. Fig. 4 shows the XRD patterns of the synthesized ZrO<sub>2</sub> nanopowder calcined at three different temperatures, 700, 800, and 900 °C. Fig. 5

shows the XRD patterns of the synthesized ZrO<sub>2</sub> nanopowder doped with 20 mol% Ni and calcined at three different temperatures, 700, 800, and 900 °C. Fig. 6 shows the XRD patterns of the synthesized ZrO<sub>2</sub> nanopowder doped with 40 mol% Ni and calcined at three different temperatures, 700, 800, and 900 °C.

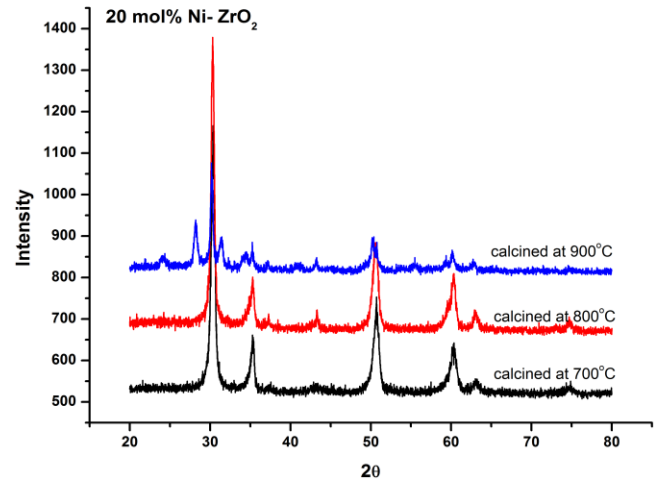


Figure 5. XRD patterns of 20 mol% Ni doped ZrO<sub>2</sub> calcined at different temperatures

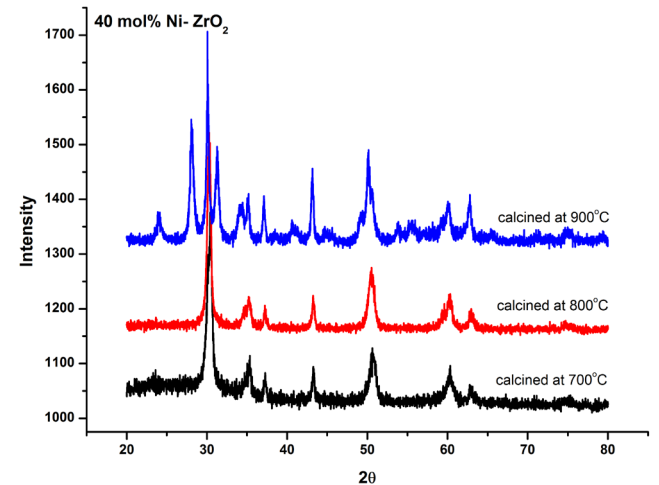


Figure 6. XRD patterns of 40 mol% Ni doped ZrO<sub>2</sub> calcined at different temperatures

At 700 °C calcination temperature, it is quite clear that the presence of monoclinic phase in pure zirconia powder is dominant. The crystallite NiO peaks were observed as a second phase at  $2\theta = 36.83^\circ$ ,  $42.88^\circ$ , and  $62.52^\circ$ . From XRD pattern, it is clearly shown that the monoclinic phase in as prepared zirconia powder is dominant. With the addition of 20 mol% of nickel, the monoclinic phase was suppressed and the tetragonal phase was enhanced. Development of NiO along with t-ZrO<sub>2</sub> was observed for 40 mol% Ni doped ZrO<sub>2</sub> powders. The crystallite size of pure zirconia, 20 mol% and 40 mol% nickel doped ZrO<sub>2</sub> was calculated using scherrer's formula and was found to be 46.3 nm, 27.8 nm, and 139.5 nm respectively.

At 800°C calcination temperature, it is quite clear that in pure zirconia powder the presence of monoclinic phase is dominant. With 20 mol% addition of nickel, the monoclinic phase was suppressed and the tetragonal phase has been enhanced. Further addition of Ni, i.e. 40 mol%, leads to development of NiO along with t-  $\text{ZrO}_2$ . By using scherrer's formula, the crystallite size of pure zirconia, 20 mol%, and 40 mol% nickel doped  $\text{ZrO}_2$  was calculated and found to be 24.4nm, 27.8 nm and 22nm respectively.

While at 900°C calcination temperature and 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% monoclinic and ~1% tetragonal). At 20 mol% Ni addition the monoclinic phase suppressed to ~60 vol % and tetragonal phase developed to ~60 vol % with presence of minor amount of NiO phase (~5 vol%). Further addition of nickel concentration leads to a decrease in tetragonal phase and an increase in monoclinic as well increase of NiO phase. This may be explained as follows: the increased concentration of dopant NiO helps nucleation of crystallites and enhances grain growth, the grain size was found to be larger in 40 mol% compared to other composition of powders. Higher grain size is inversely proportional to surface area so reduced reactivity. Crystallite size of pure zirconia, 20 mol% and 40 mol% nickel doped  $\text{ZrO}_2$  were calculated using scherrer's formula and found to be 37.7nm, 37.9 nm and 59.6 nm respectively.

Here we may conclude that at higher concentration of Ni in Ni- $\text{ZrO}_2$  composite which is calcined at high temperature, tetragonal phase of  $\text{ZrO}_2$  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.

### 3.3. IR spectroscopy

Infra-Red spectra in the range of 500-4000  $\text{cm}^{-1}$  for the as-prepared  $\text{ZrO}_2$  as well as the Ni doped  $\text{ZrO}_2$  powders with different concentrations were observed. Figure 7 shows the typical IR spectra of both the as-prepared  $\text{ZrO}_2$  and that calcined at 800°C. On the other hand, figure 8 shows the IR spectra of both the as-prepared 20 mol% Ni doped  $\text{ZrO}_2$  and that calcined at 800°C.

From the IR spectras, it is clearly shown that the as-prepared powders reveal that the  $\text{ZrO}_2$  nano powders have a significant amount of surface-adsorbed  $\text{H}_2\text{O}$  molecules has been assigned at 3401 and 3446  $\text{cm}^{-1}$  for the as prepared and the calcined  $\text{ZrO}_2$  respectively. While the as-prepared  $\text{ZrO}_2$  as well as Ni doped  $\text{ZrO}_2$  that calcined at 800°C shows Zr-O vibration as observed at 740 and 680  $\text{cm}^{-1}$ .

The size, shape and agglomeration behaviour of Ni doped  $\text{ZrO}_2$  was obtained by using scanning electron microscopy (SEM). Fig. 9 (a), (b) and (c) show the microstructural SEM secondary and backscattered images of the as prepared  $\text{ZrO}_2$ , 20 mol% Ni doped  $\text{ZrO}_2$ , and 40 mol% Ni doped  $\text{ZrO}_2$  powder respectively. The particle size was found to be nearly spherical and agglomerate in nature.

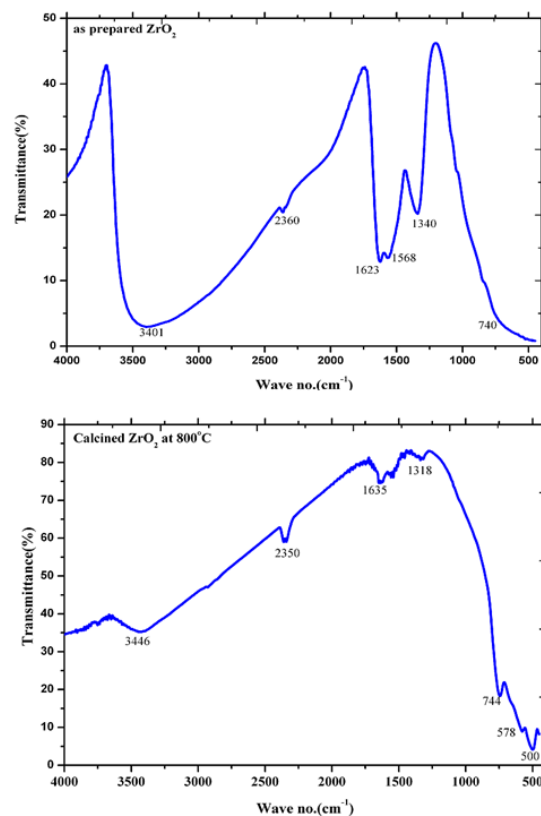


Figure 7. IR spectra of as-prepared  $\text{ZrO}_2$  and calcined  $\text{ZrO}_2$  at 800°C

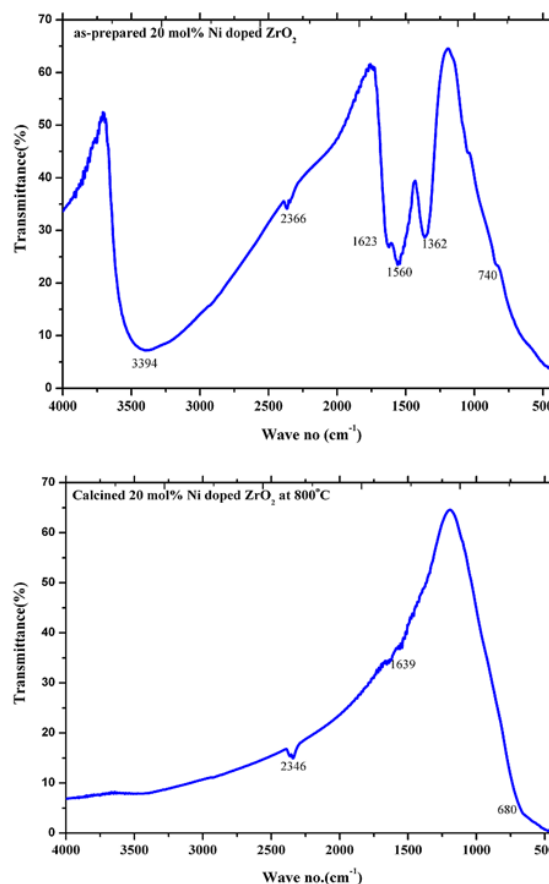
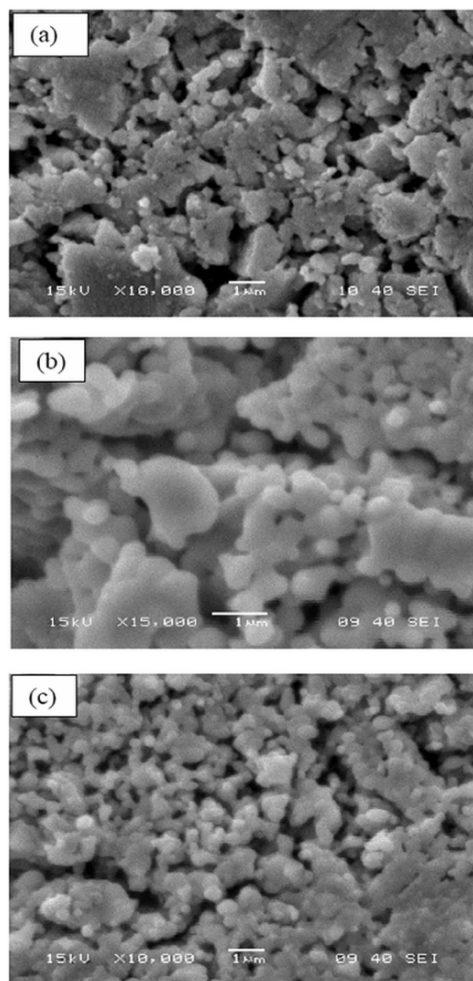


Figure 8. IR spectra of as-prepared 20 mol% Ni doped  $\text{ZrO}_2$  and calcined 20 mol% Ni doped  $\text{ZrO}_2$  at 800°C



**Figure 9.** SEM images of (a)  $\text{ZrO}_2$ , (b) 20 mol % Ni doped  $\text{ZrO}_2$ , and (c) 40 mol % Ni doped  $\text{ZrO}_2$

## 4. Conclusions

Co-precipitation route using  $\text{NH}_4\text{OH}$  has been successfully employed to synthesis nanocrystalline Ni-ZrO<sub>2</sub> powder for SOFCs. Characterization by X-ray diffraction and IR spectroscopy confirmed the presence of nanocrystallite phases of NiO and  $\text{ZrO}_2$ . Stabilization of metastable t- $\text{ZrO}_2$  is observed at 20 mol% of nickel salt at a calcination temperature of 800°C. From XRD results it has been concluded that small crystallites (27.8 nm) stabilizes metastable t- $\text{ZrO}_2$  at intermediate temperature range. Due to the presence of lattice strain above a certain concentration of nickel salt, there is decrease in tetragonal phase.

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