Room Temperature Magnetic Behavior In Nanocrystalline Ni-Doped Zro₂ By Microwave-Assisted Polyol Synthesis

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Abstract. This article, deals with a microwave-assisted polyol method to demonstrate a low temperature route < 250°C, to prepare a high temperature cubic zirconia phase. Powder XRD pattern shows broad diffraction peaks suggesting nanometric size of the particles. Magnetic behavior of 1-5 at% Ni doped samples show a threshold for substitutional induced room temperature ferromagnetism up to 3 at% of Ni. TGA data reveals that Ni-doped ZrO₂ polyol precursors decompose exothermically below 300°C. IR data confirms the reduction of Zr(OH)₄ precipitates to ZrO₂, in agreement with the conclusions drawn from the TGA analysis.

1. Introduction
Zirconia (ZrO₂) is a well-known ceramic material and has found applications in a number of technologies [1-8]. Of the three polymorphs of ZrO₂ namely cubic, tetragonal and monoclinic phases, ZrO₂cubic is the most coveted phase. Stabilization of this high temperature phase at room temperature is achieved by doping Y³⁺, Mg²⁺ and Ca²⁺ ions. There is extensive documentation of different chemical approaches to prepare stabilized ZrO₂ [10-17]. Emphasis of these approaches are aimed at (i) stabilizing ZrO₂ phase at low temperature (ii) quick processing route (iii) preparing spherical particles with narrow size distribution (iv) better sintering characteristics. Recent report on Co: ZrO₂ [18] and Fe: ZrO₂ [19] cermet nanocomposites synthesized by solution combustion method show distinct magnetization. The origin of room temperature ferromagnetism in sufficiently lean compositions of Ni, <5% is a puzzling phenomena compared to the traditionally investigated cermet compositions, Ni-doped Zirconia in the range of 10-40 at% of Nickel. This present study is an effort to understand if the magnetic behavior arises from a substitutionally induced effect. Polyol synthesis is a kinetically controlled synthesis. We report the low temperature synthesis and characterization of high temperature cubic phase ZrO₂ via microwave-assisted polyol (MAP) route. We have attempted to probe the magnetic properties of ZrO₂: Ni compositions with Ni lean composition (<5%) from the point of view of spintronics application. The polyol synthesis is assisted by a commercial microwave reactor [20].

2. Experimental
Microwave-assisted polyol (MAP) synthesis was carried out in “Discoverer” microwave reactor CEM Inc., USA. The precise control of the reaction temperature was achieved with the reactor by varying the power level. In a typical reaction, stoichiometric amounts of Zirconyl Nitrate (6.936g), Nickel Nitrate (0.0703g, 0.2145g & 0.365g for 1, 3 & 5 at% Ni-doping respectively) and Urea (3.028g) were dissolved in ~10ml of water and mixed with ~40 ml of ethylene glycol. The reaction mixture was refluxed upon microwave exposure, with a power output of 150-200 W, at ~140°C temperature. After
6hrs. of reaction, the solution was cooled and the resultant pale white precipitate was filtered, washed with ethanol several times and then dried. The precipitate obtained was then calcined at 600°C for 6 hrs. The bulk powder obtained were then characterized by X-ray diffraction, TG-DTA, scanning electron microscopy (SEM), magnetization (M) vs. magnetic field (H) measurements was taken using a vibrating sample magnetometer (DMS ADE-EV7 model).

3. Results and Discussion
Firstly, we provide an insight to the mechanism of the microwave coupled polyol synthesis route employed here. Microwave combustion method is a high temperature fast quenching route. The polyol synthesis is a wet chemical synthesis involving high boiling alcohols with multiple hydroxyl groups. The polyol route has been employed for two decades to prepare metals, alloys and oxides in nano- and sub-micron particle size regime [24-25]. The alcohol employed serves as a solvent as well as a reducing agent to reduce the metal ion to metal particle. The mechanism of the polyol mediated reaction involves two stages i.e. (i) formation/ crystallization of the metal hydroxide (ii) formation of metal particles/ oxides depending on the nature of the element. Further reaction continues as spontaneous nucleation and growth of metal particles, where temperature affects the growth kinetics.

![Schematic flow chart for synthesis of Ni-doped ZrO2](image)

- ZrO(NO3)2·H2O
- Ethylene Glycol
- NH2CONH2
- Ni(NO3)2·H2O

**Precipitation**

- Washed with Ethanol
- Dried in oven at 80°C for 30 hrs.
- Crushing and grinding
- Calcined at 600°C for 6 hrs.

**Characterization (XRD, IR, TGA-DSC, VSM)**
The application of microwave along with polyol is advantageous in reducing the time scale of the conventional wet chemical route where polyol acts as a good microwave absorber. Microwave coupled polyol synthesis is a soft chemical route that predominantly leads to the formation of amorphous Zr(OH)$_2$ phase. These as-prepared precipitates are X-ray amorphous, which on heating (600°C, 6hrs.), give single phase cubic- ZrO$_2$: Ni nanoparticles.

![X-ray powder diffraction pattern of as prepared Ni-doped ZrO$_2$. The miller indices refer to the cubic fluorite-type ZrO$_2$ structure.](image)

**Table 1:** Variation of lattice parameter (Å) and crystallite size (nm) with Ni conc. (x).

| Zr$_{1-x}$Ni$_x$O$_2$ | Ni conc. (x) | ‘2θ’ (deg.) | Lattice parameter ‘a’ (Å) | Crystallite Size (nm) |
|----------------------|-------------|-------------|--------------------------|---------------------|
|                      | 0           | 30.178      | 5.125                    | 11.73               |
|                      | 0.01        | 30.193      | 5.123                    | 10.82               |
|                      | 0.02        | 30.205      | 5.121                    | 10.61               |
|                      | 0.03        | 30.221      | 5.118                    | 11.26               |
|                      | 0.04        | 30.212      | 5.119                    | 11.98               |
|                      | 0.05        | 30.211      | 5.119                    | 10.06               |

Figure 1 shows the powder X-ray diffraction patterns of the 0-5 at% Ni/ZrO$_2$ compositions. All the compositions crystallize in cubic phase and show broad diffraction peaks due to nanometric size, when
prepared by microwave–assisted polyol (MAP) route. This is noteworthy since conventional wet route synthesized ZrO$_2$ samples do not crystallize in cubic phase, as a result, stabilizing agents like Yttria, Calcia and Magnesia are added to stabilize cubic zirconia phase. The samples studied do not show additional reflections of any crystalline impurities and with increase in Ni-doping, the intensity of the peaks goes on increasing, which indicates that with increase in Ni-doping, the cubic phase of ZrO$_2$ gets more stabilized. Small angular displacement of each peak in the XRD pattern with respect to the bulk zirconium dioxide has been observed in the Ni-doped ZrO$_2$ sample (cf. Table 1). There is a shift in 20 values of peaks towards higher angle up to 3 at% Ni-doping and this may be attributed to the contraction of the cubic lattice caused by the smaller dopant of Ni$^{2+}$ ion in the ZrO$_2$ lattice. The average particle size of all the samples are evaluated from the Debye-Scherrer equation $<D> = 0.89 \lambda / \beta^{1/2} \cos \theta$, where $<D>$ is the average particle size, $\lambda$ is the wavelength of the incident X-ray, $\theta$ is the corresponding Bragg angle and $\beta^{1/2}$ is the full width at half maxima (FWHM) of the XRD peak. The uncertainties in the particle size determination were estimated from the errors in the fitting procedures, which lie in the range ±1nm. The average particle sizes of all the samples are in the range 10 - 12 nm (cf. Table 1).

The lattice parameters are calculated using the XRD pattern (cf. Table 1). The variation of lattice parameter ‘a’ with Ni conc. ‘x’ of the as-prepared samples are given in figure 2, which shows a contraction in the lattice results up to 3 at% of Ni doping, keeping the cubic symmetry intact. Such lattice contractions may be an aftermath of short range ordering of oxygen vacancies to relax the structural strain. In other words, the incorporation of substituent atom of size different from Zr$^{4+}$ generates lattice strain and oxygen vacancies (if the substituent is of lower valency) [26]. In cubic ZrO$_2$, if Ni is assumed to be replacing Zr$^{4+}$, the reported Ni ion is Ni$^{2+}$. The presence of Ni$^{2+}$ impurity in the samples may be considered as an evidence for this assumption. Here Ni$^{2+}$ is smaller than Zr$^{4+}$ and can naturally generate strain in the lattice. In short, the contraction of the lattice of

![Figure 2](image_url). Shows the variation of lattice parameters with % Ni concentration (x). Note that a contraction in the lattice results for compositions up to 3 at% of Ni-doping.
Zr$_{1-x}$Ni$_x$O$_2$ compositions can be due to the substitution of Ni$^{2+}$ in Zr$^{4+}$ site. Beyond 3 at% Ni doping, there is no more substitution as there is no more contraction in the lattice and it could result in Ni converted to NiO phase.

Figure 3. Shows the TGA curve of Zr$_{1-x}$Ni$_x$O$_2$ (0 < x < 0.05) samples. TG analysis is made in nitrogen gas flow at a heating rate of 5$^\circ$C/min.

Figure 4. Shows the DSC curves of Zr$_{1-x}$Ni$_x$O$_2$ (0 < x < 0.05) samples. DSC analysis is made in nitrogen gas flow at a heating rate of 5$^\circ$C/min.
The thermal behavior of the gel-like mass produced at 140°C was studied up to 600°C using thermogravimetric analysis (TGA). The TG curve depicted in Figure 3 shows weight loss up to 210°C. This gives clue to decide on the final calcination temperature to be 250°C. It is well known that in the preparation of nano-sized ZrO$_2$ different hydroxide entities are originated depending on the Zr concentration. The aforementioned TG data show a mass loss of about 56% which could be assigned to the thermal dehydration of Zr(OH)$_4$.6H$_2$O to yield ZrO$_2$ and H$_2$O. In this conversation, the remaining mass of ZrO$_2$ is 44% being equal to that observed in TG. However, it has to be stated that this agreement is just an indication for Zr(OH)$_4$.6H$_2$O, whereas additional analytical methods are necessary to unambiguously prove the structure of the Zr species.

**Figure 5.** Shows X–ray diffraction patterns and Infrared spectra of as prepared ZrO$_2$ and 2 atom% Ni-doped ZrO$_2$ as well as of calcined samples at 250°C for 2 hrs.

In case of pure ZrO$_2$, the TGA shows initial weight loss below 150°C due to elimination of water. Then the sharp weight loss at 160°C is due to the decomposition of Zirconium hydroxide to ZrO$_2$. In differential scanning calorimetry (DSC), the sharp exothermic peak at this temperature is due to the phase transition of amorphous Zr(OH)$_2$ phase to cubic ZrO$_2$ phase. However, it is of interest to see the influence of Ni-doping on the crystallization of ZrO$_2$ from amorphous to cubic phase. In Figure 4, this peak is shifted to higher temperature due to the doping of Ni in ZrO$_2$. Consequently, the exothermic peaks appear at 160°C for ZrO$_2$, 190°C for 1 at% Ni-doped ZrO$_2$, 210°C for 3 at% Ni-doped ZrO$_2$. The decomposition temperature depends on the amount of Ni-doping. The temperature increases with increasing Ni-content up to 3 at%, indicating an increase in thermal stability of ZrO$_2$ with Ni content up to 3 at%. For 5 at% Ni- doped ZrO$_2$, the temperature again falls back to that of ZrO$_2$, indicating that...
there is no more Ni-doping and the extra Nickel doped might be getting converted to NiO, which is responsible for decrease in magnetic moment in magnetization plot as NiO shows antiferromagnetic behavior.

**Figure 6.** Shows X–ray diffraction patterns and Infrared spectra of ZrO$_2$ and 2 atom % Ni-doped ZrO$_2$ samples calcined at 400 and 600 °C for 2 hrs.

Figure 5 (a & c) shows the XRD patterns of as-prepared and calcined (at 250°C) samples of ZrO$_2$ and 2 atom% Ni-doped ZrO$_2$. As prepared samples are amorphous, indicating corresponding hydroxides whereas 250°C calcined samples show semi crystalline behavior and broad peaks indicate the smaller particle size of the material. Figure 5 (b & d) shows the corresponding infrared spectra (IR) spectra (in the range 400 - 4000 cm$^{-1}$) of ZrO$_2$ and Ni-doped ZrO$_2$ sample. The spectra show two broad bands at 3500 and 3200 cm$^{-1}$, which suggests the presence of corresponding hydroxides associated with significant amount of H$_2$O molecules. When the samples are calcined at 250°C, the band due to H$_2$O molecule becomes weaker whereas the Zr-O vibration band became prominent.

As we calcine the samples at 400°C (Figure 6. (a) & (b)), the XRD pattern became more crystalline with broad peaks indicating the smaller particle size and in IR, the band due to H$_2$O molecule almost gets eliminated and the Zr-O vibration band gets more intensified. In case of 600°C calcined samples (Figure 6 (c) & (d)), the peaks are perfectly crystalline corresponding to the cubic phase of pure ZrO$_2$ and the sharper peaks indicate bigger particle size as compared to that of 400°C calcined samples. In IR, the H$_2$O molecules get completely eliminated indicating the pure phase of ZrO$_2$. 

The M vs. H hysteresis loops of $\text{Zr}_{1-x}\text{Ni}_x\text{O}_2$ compositions ($0.0 < x < 0.05$) at room temperature is presented in Figure 7. This shows an increase in moment with increase in Ni concentration up to 3 at%, with ferromagnetic behavior, whereas for 4 & 5 at% of Ni, there is decrease in magnetic moment with paramagnetic behavior. The inset to Figure 7 shows the M vs. H loop of parent $\text{ZrO}_2$ bulk sample, which shows a diamagnetic behavior. On the other hand, we observe room temperature ferromagnetic signal for low percentage of Ni-doping up to 3 at%. This ensures that the ferromagnetism is because of Ni-doping only and may be Ni$^{2+}$ is getting substituted in Zr$^{4+}$ site. Whereas the decrease in magnetization beyond 3 at% of Ni could be due to the formation of antiferromagnetic NiO phase. This reveals that, the solubility limit of Ni in cubic $\text{ZrO}_2$ lattice is up to 3 at%.

**Figure 7.** Shows comparison of hysteresis of $\text{Zr}_{1-x}\text{Ni}_x\text{O}_2$ ($0.0 < x < 0.05$) compositions at room temperature. Inset shows the M vs. H plot of the parent $\text{ZrO}_2$ at room temperature.

4. **Conclusion**
We report a microwave assisted polyol method to demonstrate a low temperature route $<$300$^\circ$C, to prepare cubic zirconia phase. Magnetic behavior of 1-5 at% Ni doped samples show a threshold for substitutional induced room temperature ferromagnetism up to 3 at% of Ni. TGA data reveals increase in Ni-doping, increases the thermal stability of cubic $\text{ZrO}_2$, up to 3 at% of Ni. IR data confirms the reduction of $\text{Zr(OH)}_4$ precipitates to $\text{ZrO}_2$, which is in agreement with that of the conclusions drawn from TG analysis.

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