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Synthesis of Mg^{2+} doped NiO nanoparticles and their structural and optical properties by Co-precipitation method

M. Karthikeyan[1], P. Vijaya Kumar*[2], A. Jafar Ahamed[3] and A. Ravikumar[1]

[1]Department of Chemistry, Periyar Maniammai Institute of Science and Technology, Vallam, Thanjavur-613 403, Tamil Nadu, India.

[2]Department of Chemistry, Jairams Arts and Science College, Affiliated to Bharathidasan University, Karur- 639 003, Tamil Nadu, India.

[3]Post Graduate and Research Department of Chemistry, Jamal Mohamed College (Autonomous), Affiliated to Bharathidasan University, Tiruchirappalli - 620 020, Tamil Nadu, India.

***Corresponding Author** E mail ID: pdvijayjmc@gmail.com

Abstract:

Nanocrystalline Magnesium-doped NiO nanoparticles (Mg^{2+} doped NiO NPs) were synthesized by co-precipitation method. The prepared samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet- visible spectrometer (UV-Vis) and Tunneling electron microscopy (TEM) with EDAX specifications. XRD pattern reveals that Mg^{2+} doped NiO nanoparticles belongs to the face centered cubic crystal structure with the space group of Fm-3m. Electron microscopy studies clearly evidence the formation of cubical edged nanoparticles with an average particle size of 21.49 nm, emerges in the polycrystalline nature. UV-Visible absorption spectra of Mg^{2+} doped NiO nanocrystals shows an absorption peak at 289nm. The bandgap value is calculated to be 4.8 eV.

Keywords: Nanoparticles, Co-precipitation method, Optical studies and morphological analysis.

1. Introduction:

One of the most commonly used transition metal oxides for a wide range of applications is NiO. It is a NaCl-type anti-ferromagnetic oxide semiconductor. Furthermore, it is considered to be a model semiconductor with p-type conductivity films due to its wide band gap [1]. Uniformly sized with well dispersed NiO nanoparticles as a kind of functional material has attracted extensive interests due to its novel optical, electronic, magnetic, thermal and mechanical properties and potential applications in catalysis, battery electrodes, gas sensors, electro chromic films, photo electronic devices, magnetic materials and so on [2-7]. In these applications, it is still needed for synthesizing high quality and ultra- fine powders with required characteristics in terms of their size, morphology, optical properties, magnetic properties and so on.

Several methods have been used and developed for synthesizing crystalline oxide powders in nanoscale dimensions. In many of them, the main objective is to reduce the cost of chemical synthesis and to produce materials for technological applications. Many researchers have employed NiO nanoparticles by various methods such as evaporation [8-9], magnetron sputtering [10-12], sol-gel [13-14], surfactant-meditated synthesis [15], thermal decomposition [16], solvothermal [17], polymer-matrix assisted synthesis [18] and so on. Among various methods, the preparation of Magnesium-doped NiO nanostructures through Co-precipitation method open a new view for chemists since there are many advantages such as simple process, control of process conditions, particle size, particle crystal structure and easiness to obtain high purity products. Hence it is quite promising and easy to use for industrial applications. NiO is a most exhaustively investigated transition metal oxide.

In the present work, we report that Mg^{2+} doped NiO NPs were synthesized by chemical co-precipitation method and their structural and optical properties have been investigated.

2. Experimental Method

0.09 M of nickel nitrate hexahydrate, 0.01M of magnesium nitrate hexahydrate solution and 0.8M of NaOH were separately dissolved in each 100 ml of distilled water using three 200 ml beakers. At first, nickel nitrate and magnesium nitrate solutions were mixed homogenously. Then, NaOH solution was added drop wise to the homogenous mixed solution which yields a green

precipitate. The solution with the green precipitate was stirred at room temperature for 30 min, and then at temperature of 60 ^{o}C for 4 h. This solution was refluxed at room temperature for 24 h. Then, a clear solution was obtained, which found to be stable at ambient condition. Thereafter, the solution was washed several times with double distilled water and ethanol. Finally, the precipitate was dried at 120 °C. Thus, Mg^{2+} doped NiO sample was obtained. This sample was annealed at 600 ^{o}C for 4 h because the energy from the heat can enhance the vibration and diffusion of lattice atoms for crystallization.

2.1. Characterization Studies:

The phase purity of the synthesized NPs were determined by X-ray diffractometer (Model: X'PERT PRO PAN analytical). The morphology of the synthesized Mg^{2+} doped NiO NPs was examined using HRTEM. Sample for HRTEM analysis was prepared by drop coating the nanoparticles solutions on carbon-coated copper grids at room temperature. The excess nanoparticles solutions were removed with filter paper. The copper grid was finally dried at room temperature and was subjected to TEM analysis by the instrument Tecnai F20 model operated at an accelerating voltage of 200 kV. The samples were analyzed by EDAX (model: ULTRA 55). The vibrational frequency was measured by Fourier transform infra-red spectroscopy (Perkin-Elemer). The absorption spectrum of the sample was measured on Perkin-Elmer (Lambda 35).

3. Results and Discussion:

3.1. XRD analysis for Mg^{2+} doped NiO Nanoparticles

The X-ray diffraction pattern of synthesized Mg^{2+} doped NiO NPs are shown in Fig 1. The XRD peaks are obtained at angles (2θ) of 37.26˚, 43.50˚, 63.08˚, 75.39˚ and 79.50˚ corresponding to (111), (200), (220), (311), and (222) planes, and very good accordance with a cubic NiO crystal structure (JCPDS Card No: 78-0643: space group = Fm3/m). It is also observed that there is no impurity phase found in the Mg^{2+} NiO samples, because of ionic radii of Mg (0.66 Å) is below than Ni (0.69 Å). The lattice constants 'a', 'b' and 'c' of NiO NPs can be calculated by using the following relation.

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \text{---------- (1)}$$

The calculated lattice constant value of a = b = c = 4.1605 Å, it is closely related to the standard lattice constant value of a = 4.176 Å. Moreover, no other peak is observed belonging to any adsorbed impurities or phase such as $Ni(OH)_2$, NiO_2, $NiCO_3$. Thus the XRD studies confirm the absolute transformation to NiO. The grain size of the crystallites of as synthesized product was calculated using Debye-Scherrer formula.

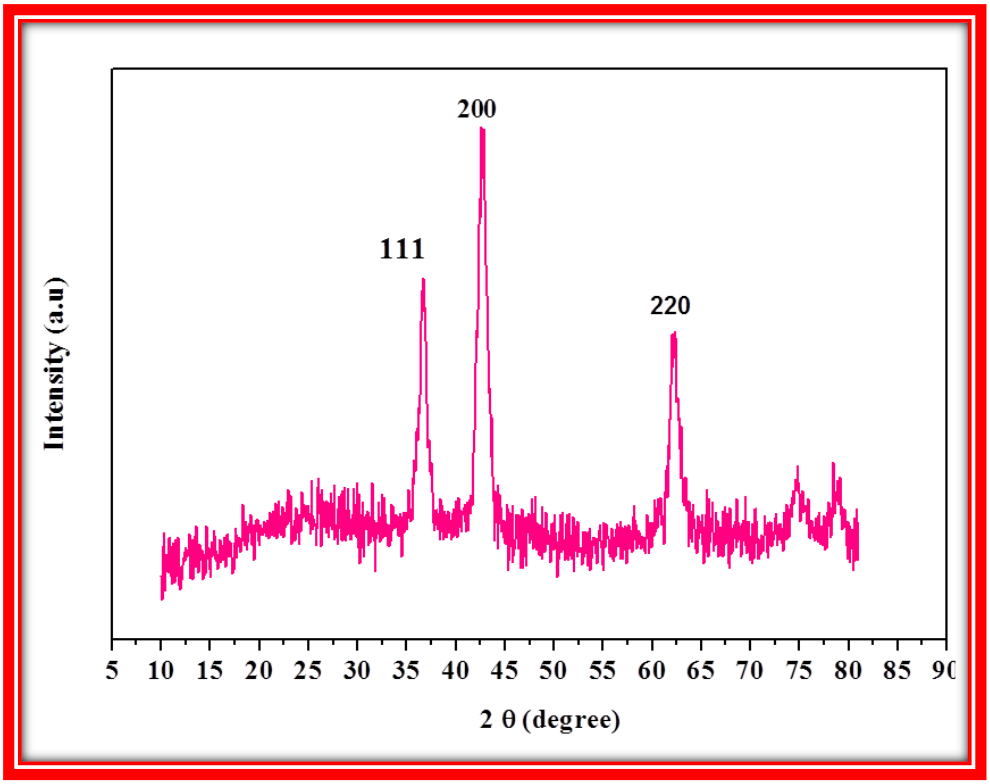


Figure 1: XRD pattern of Mg^{2+} doped NiO Nanoparticles

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \text{ ---------} \quad (2)$$

Where λ is the wavelength of X-ray used (0.15418nm in the present case), β is the full width in radiation at half-maximum of the peak, and θ is the Bragg angle of X-ray diffraction peak. The average crystallite size of the as synthesized nanoparticles was 21.49 nm.

3.2 Morphological studies of Mg^{2+} doped NiO nanoparticles

The surface morphology of Mg^{2+} doped NiO nanoparticles is examined by tunnelling electron microscopy results. Figure 2 (a) shows the TEM image of synthesized Mg doped NiO nanoparticles. From the figure, the surface is observed to be smooth and covered with uniform rod like shaped particles and also, we observed the

agglomerated particles due to surfactant free synthesis of Mg^{2+} doped NiO nanoparticles. The grains are distributed uniformly over the entire surface of the Nanoparticles. The sizes of grains are found to be in the range between 20 nm and 30 nm. The average size of the grains is found to be 21 nm and it is in good agreement with the XRD results.

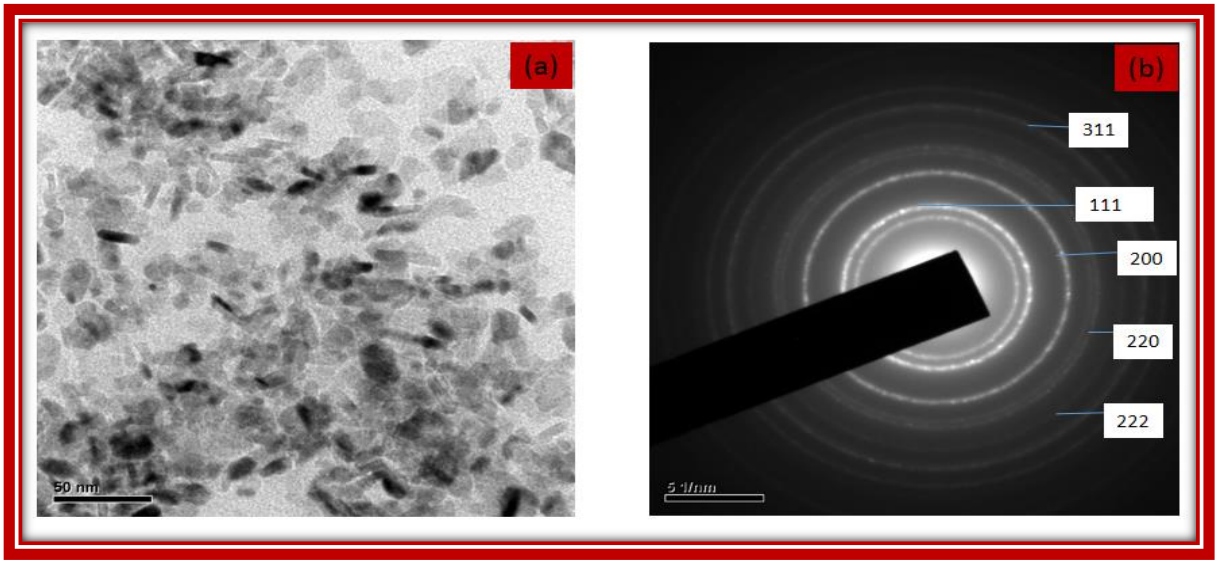
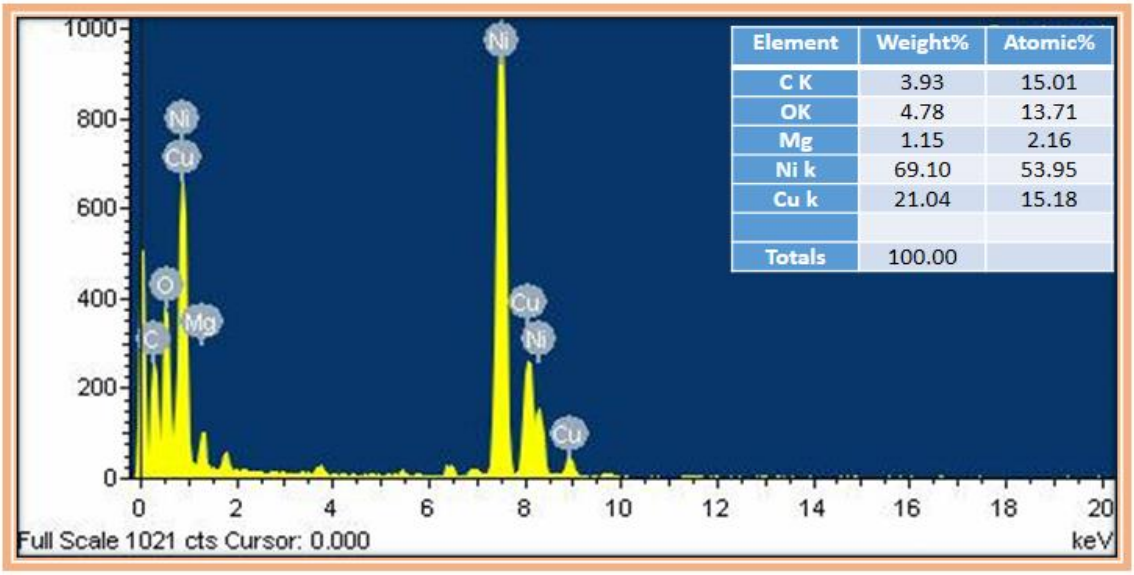


Figure 2 (a) HRTEM image Figure 2 (b) SAED studies of Mg^{2+} doped NiO nanoparticles

The crystallinity of the synthesized Mg^{2+} doped NiO NPs was examined by selected area diffraction studies. Figure 2 (b) shows the nano rod like structure with regular spacing of clear lattice planes.

3.3 Energy dispersive analysis X-ray (EDAX) studies



The quantitative analysis of the synthesized samples was carried out by using the Energy dispersive analysis of X-ray technique to study.

Figure 3 shows typical EDAX pattern of the Mg^{2+} doped NiO nanoparticles. The EDAX data clearly indicates that the elements Ni, Mg, O present in the sample and the weight percentages are Ni = 53.95%, Mg = 2.16%, O = 15.01% and there was no impurities present in the sample.

Figure 3. EDAX spectrum of Mg^{2+}doped NiO nanoparticles

3.4 Fourier Transform Infra-Red (FT-IR) Spectroscopic Analysis

FT-IR spectroscopic analysis reveals that the vibrational frequencies of the alkaline metal ion (Mg^{2+}) doped NiO NPs. The recorded FT-IR spectrum is shown in figure 4. The absorption band at 3457 cm^{-1} and the weak peak at 2909 cm^{-1} are assigned to OH stretching and bending modes of water, respectively [19]. The peak at 1421 cm^{-1} is attributed to the stretching vibration of the metal oxide crystallites of Mg and Ni [20]. The peak observed at 489 cm^{-1}, which correspond to Ni-O nanoparticles stretching mode [21].

3.5 UV-visible studies of Mg^{2+} doped NiO nanoparticles

Figure 5 demonstrates the UV-visible spectrum of the Mg^{2+} doped NiO nanoparticles suspension as obtained by ultrasonic dispersion in water. A strong absorption peak in the UV region is observed at wavelength of 289 nm.

Figure 6 displays the band gap spectrum of Mg^{2+} doped NiO nanoparticles. The absorption band gap (E_g) is usually achieved with the aid of the following equation.

$$\alpha = \frac{k\,(h\upsilon - E_g)^{n/2}}{h\upsilon} \text{---------- (3)}$$

Where k is a constant, E_g is the band gap and n is a constant equal to 1 for direct gap semiconductors and 4 for indirect band gap semiconductors materials.

The variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ is linear at the absorption edge which confirmed direct band gap transition in Mg^{2+} doped NiO.

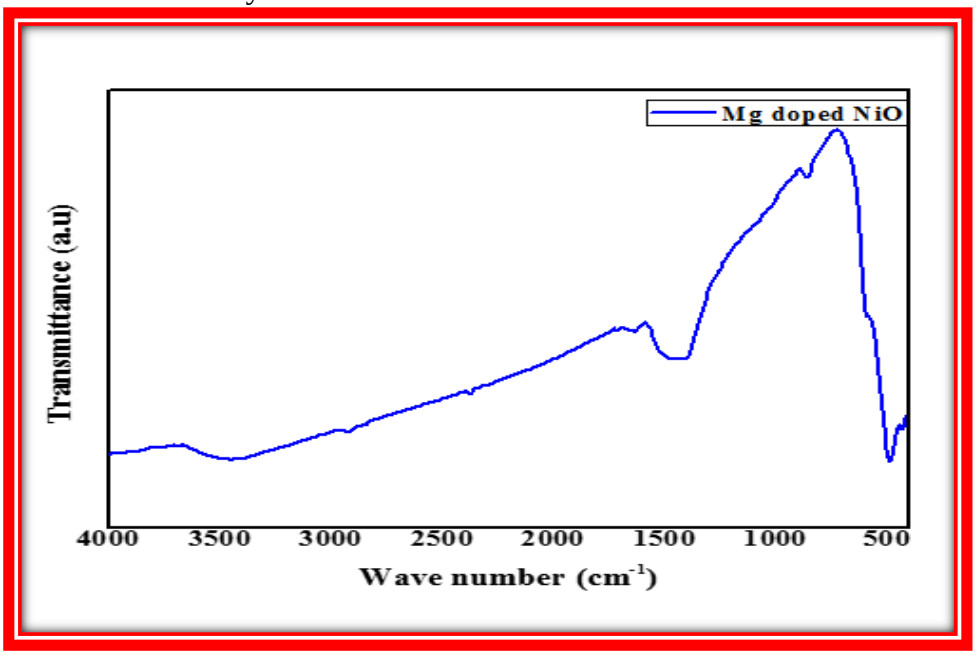


Figure 4. FTIR spectrum of Mg^{2+} doped NiO nanoparticles

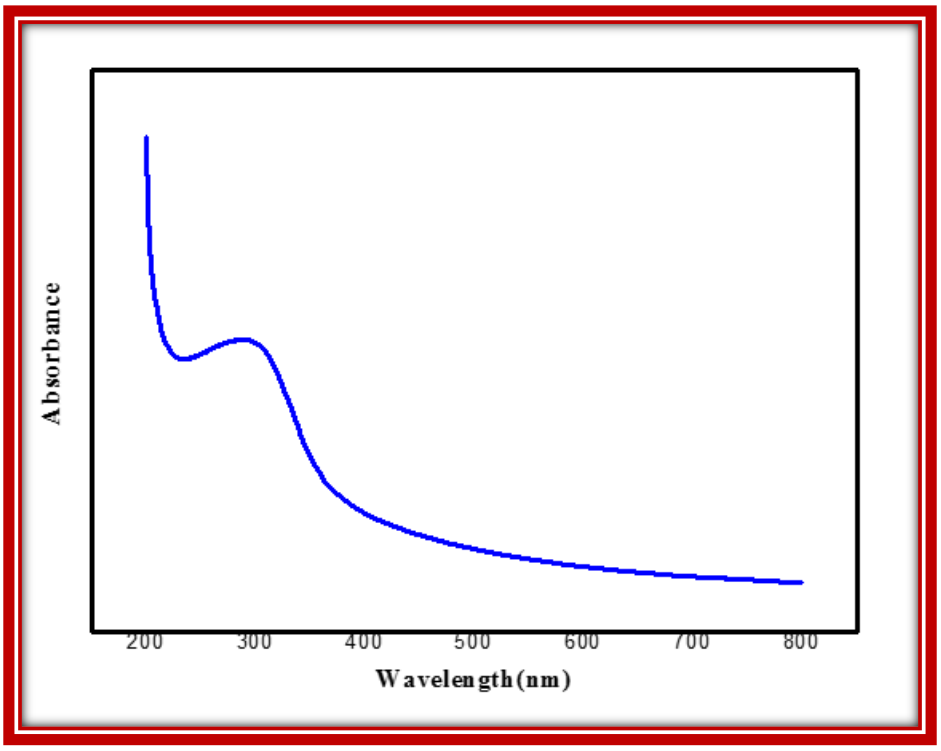


Figure 5. UV-vis spectrum of Mg^{2+} doped NiO nanoparticles

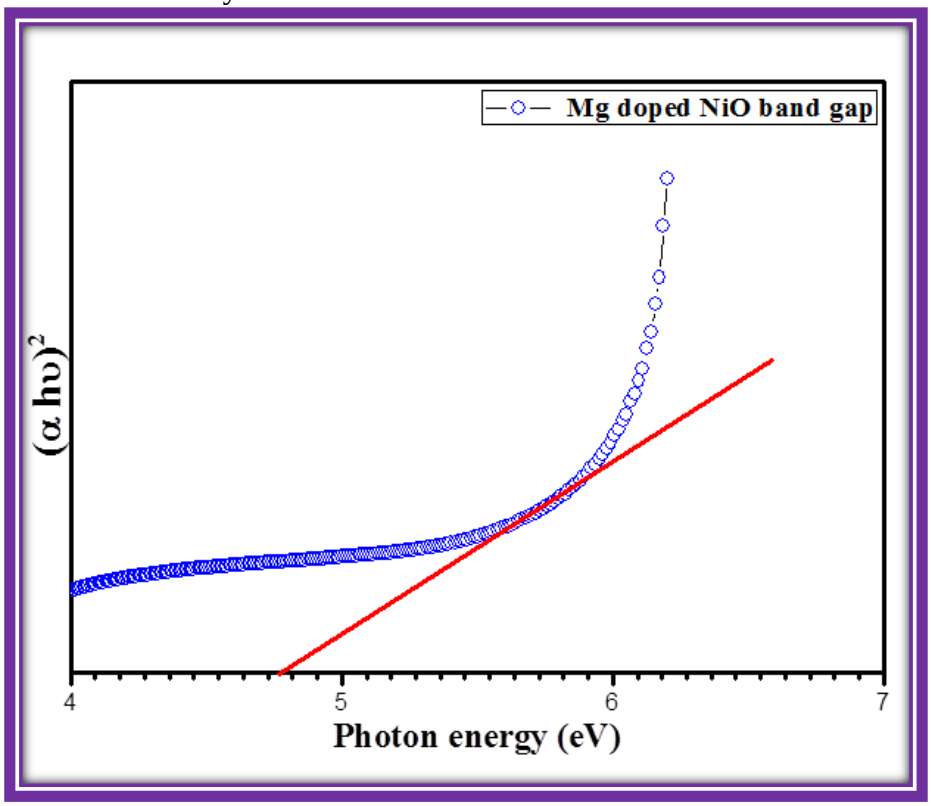


Figure 6: Band Spectrum of Mg^{2+} doped NiO nanoparticles

The band-gap energy of the as-prepared Mg^{2+} doped NiO nanoparticles is found to be 4.8 eV and it was comparatively higher than bulk value of 2.5 eV NiO. The increase in band gap of NiO nanoparticles is the inductive of quantum size effects [22].

4. Conclusion:

In summary, alkaline metal ion Mg^{2+} doped NiO nanoparticles were prepared through co-precipitation method. The X-ray diffraction study confirmed that the prepared particles were in the cubic structure with mean size of 21nm. From the HRTEM images, the particles were found to have nano rod like morphology. The EDAX analysis evident that expected elements were present in the sample. The FT-IR spectral data were assigned various vibrational frequencies for the alkaline metal ion doped NiO samples. The UV-Vis spectrum showed the optical band gap of 4.8 eV, which indicates the red shift on the size reduction. This method does not require the complexing apparatus, catalyst or any surfactant.

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