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Effect of Lithium Doping Concentration on the Structural, Morphological and Optical Properties of NiO Nanoparticles

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Abstract**—** *NiO has a wide bandgap value ranging from 3.6 to 4.0 eV and exhibits low p-type conductivity. The structural and optical properties of NiO-based nanoparticles can be modified by doping with lithium (Li) for suitable applications in the field of photocatalysis and sensors. In this present work, sol-gel method is used to produce the pure NiO nanoparticles and Li doped NiO nanoparticles at two different concentrations 0.01 M and 0.09 M. All the samples exhibit cubic structure as confirmed from the JCPDS File No.: 89-5881. The absence of impurity peaks reveals that the pure and Li doped NiO nanoparticles exhibit high crystalline quality. From PXRD and FESEM, it is observed that crystallinity and average grain size of the NiO nanoparticles increases with increase in the Li doping concentration. PL studies show a blue shift for the pure and Li doped NiO nanoparticles.*

Keywords**—** *Average grain size, blue shift, FESEM, Li doped NiO nanoparticles, PL, PXRD.*

I. INTRODUCTION

One of the most commonly used transition metal oxide for a wide of application is nickel oxide [1]. NiO nanoparticles are very prosperous materials with small dimension, high specific surface area and good chemical activity. Due to these advantages, NiO nanoparticles have extensively attracted interests in many applications, especially in catalysts, supercapacitors, battery electrodes, gas sensors etc. [2]. 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 [3]. The particle size, distribution and morphology are closely related to the preparation techniques. Many researchers have prepared NiO nanoparticles by various methods such as evaporation, magnetron sputtering, sol-gel, surfactant-meditated synthesis, thermal decomposition, solvothermal and polymer-matrix assisted synthesis [4-10]. Among various methods, the preparation of pure and Li doped NiO nanostructures by sol-gel method possess many advantages such as being simple, economic, low temperature process, versatile and flexible [11]. Undoped NiO has a wide bandgap value ranging from 3.6 to 4.0 eV and exhibits low p-type conductivity. The conduction mechanism of NiO is primarily determined by holes generated from nickel vacancies, oxygen interstitial atoms and used dopant. The resistivity of NiO-based nanoparticles can be decreased by doping with lithium (Li) [12-16]. However, only few efforts have been made to systematically investigate the effects of Li concentration on the structural and optical properties of NiO nanoparticles. In this present work, sol-gel method is used to produce the pure NiO nanoparticles and Li doped NiO nanoparticles at two different concentrations 0.01 M and 0.09 M.

II. EXPERIMENTAL TECHNIQUES

All the chemicals used are of Analytical grade.

A. Synthesis of Pure Nickel Oxide Nanoparticles

0.5 M Nickel nitrate and 0.5 M sodium hydroxide are separately dissolved in double distilled water and stirred thoroughly using magnetic stirrer. Then sodium hydroxide solution is added dropwise to the nickel nitrate solution under constant stirring. The solution is washed with double distilled water and ethanol for several times. Then it is dried in hot air oven for about 100^{o}C for 24 hours. The precipitate thus dried is kept in the muffle furnace and calcined at 300^{o}C for 2 hours.

B. Synthesis of Li Doped NiO Nanoparticles

0.5 M Nickel nitrate, 0.01 M Lithium nitrate and 0.5 M sodium hydroxide are separately dissolved in double distilled water and stirred thoroughly using magnetic stirrer. Nickel nitrate and lithium nitrate solutions are mixed thoroughly using magnetic stirrer followed by the dropwise addition of sodium hydroxide under constant stirring. The solution is washed with double distilled water and ethanol for several times. Then it is dried in hot air oven for about 100^{o}C for 24 hours. The precipitate thus dried is kept in the muffle furnace and calcined at 300^{o}C for 2 hours. The same procedure is carried out to prepare 0.09 M Li doped NiO nanoparticles.

C. Characterization

The structural analysis of the synthesized nanoparticles is performed by recording the powder X-ray diffraction (PXRD) spectrum using X-ray diffractometer (PANalytical X'Pert Pro) with Cu-K_{α} as the radiation source (wavelength: 1.54056 Å). The morphology of the samples is examined by Field Emission Scanning Electron Microscope (FESEM) JEOL JSM-6390 operating at an accelerating voltage of 20 kV. Photoluminescence (PL) studies are carried out using a photoluminescence spectrophotometer (Varian Cary Eclipse) and the spectra are recorded at a scan rate of 600 nm/min using an excitation wavelength of 270 nm.

S. Irudaya Sahaya Lancy, M. Priya Dharshini, V. Shally, and Sr. Gerardin Jayam, "Effect of lithium doping concentration on the structural, morphological and optical properties of NiO nanoparticles," *International Research Journal of Advanced Engineering and Science*, Volume 1, Issue 2, pp. 55-58, 2016.

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III. RESULTS AND DISCUSSION

The PXRD pattern for the pure NiO nanoparticles with the high intensity peaks observed at 2θ= 43.16° along the (4 0 0) hkl plane, 2θ= 62.61° along the (4 4 0) hkl plane and 2θ= 37.01 ° along the (2 2 2) hkl plane are presented in figure 1.

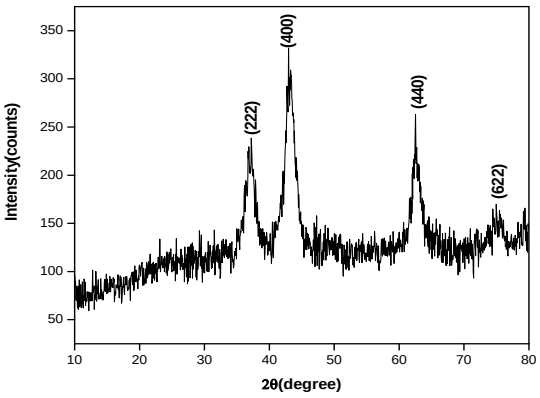

Fig. 1. PXRD pattern of pure NiO nanoparticles

The PXRD pattern for the 0.01 M Li doped NiO nanoparticles with the high intensity peaks observed at 2θ=43^0 along the (4 0 0) hkl plane, 2θ= 37.2° along the (2 2 2) hkl and 2θ= 62.9° along the (4 4 0) hkl plane are presented in Fig.2. The PXRD pattern for the 0.09 M Li doped NiO nanoparticles with the high intensity peaks observed at 2θ= 43.28° along the (4 0 0) hkl plane, 2θ= 37.25° along the (2 2 2) hkl and 2θ= 62.88° along the (4 4 0) hkl plane are shown in Fig.3. All the samples exhibit cubic structure as confirmed from the JCPDS File No.: 89-5881. The absence of impurity peaks reveals that the pure and Li doped NiO nanoparticles exhibit high crystalline quality.

Using β as the full width at half maximum (FWHM) of a broad diffraction peak, the average grain size can be estimated by applying the Scherrer's equation:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where λ is the X-ray wavelength, θ is the Bragg's angle and K is the Scherrer constant. The dislocation density is found out using the formula δ= 1/D^2 lines/m^2.

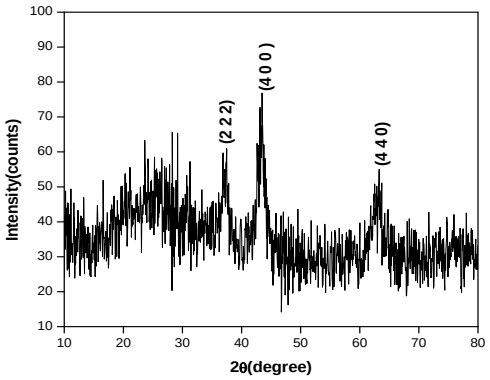

Fig. 2. PXRD pattern of 0.01 M Li doped NiO nanoparticles

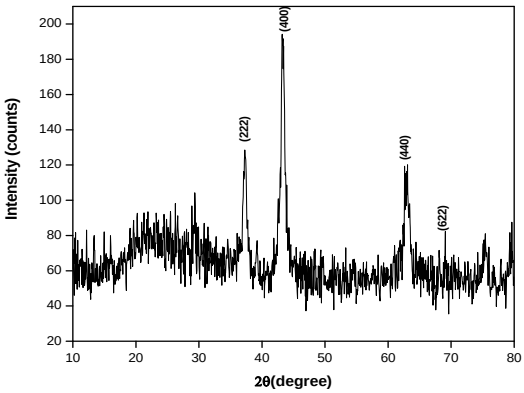

Fig. 3. PXRD pattern of 0.09 M Li doped NiO nanoparticles

TABLE I. Average grain size and dislocation density of pure and Li doped NiO nanoparticles

S. No.	Nanopowder Samples	Average Grain Size (nm)	Dislocation Density (10^{15}) (lines/m^2)
1.	Pure NiO	4.7294	0.04471
2.	0.01 M Li doped NiO	7.1940	0.01932
3.	0.09 M Li doped NiO	13.3609	0.00560

The average grain size of the pure NiO nanopowder sample is 4.7294 nm. As the Li dopant is incorporated at 0.01 M concentration, the average grain size increases to 7.1940 nm and its PXRD pattern shows slightly stronger peak intensity than that of the pure NiO nanopowder. The broad peaks reveal the polycrystalline nature of the sample. As the Li doping concentration is increased to 0.09 M, the average grain size further increases (Table I) and the sharp peaks reveal the crystalline nature of the sample. As the average grain size increases, the dislocation density of the nanopowder samples decrease. Hence as the Li doping concentration increases the average grain size and crystallinity increase, indicating that the crystallinity of NiO nanoparticles can be improved by lithium doping [17].

The surface FESEM image of pure NiO nanoparticles in figure 4 which shows a combination of small needle-like (~100 nm) and leaf-like (~67 nm) structures. The particles are essentially formed as a cluster. The FESEM picture indicates the size of polycrystalline particles. The observation of some larger nanoparticles may be attributed to the fact that NiO nanoparticles have the tendency to agglomerate due to their high surface energy and high surface tension of the ultrafine nanoparticles. The fine particle size results in a large surface area that in turn, enhances the nanoparticles catalytic activity [18].

From figure 5, it is observed that as the Li doping concentration is 0.01 M, the particles exhibit a cluster-like (each cluster size ~ 166 nm) morphology consisting of nanocrystalline grains oriented randomly. From figure 6, it is seen that as the Li doping concentration is increased to 0.09 M, the pores decreases [17]. The improved grain growth can be attributed to the small radius of the Li ions. During the crystal growth process, it is easier for these ions with low activation energy to escape from trap sites and transfer to

S. Irudaya Sahaya Lancy, M. Priya Dharshini, V. Shally, and Sr. Gerardin Jayam, "Effect of lithium doping concentration on the structural, morphological and optical properties of NiO nanoparticles," *International Research Journal of Advanced Engineering and Science*, Volume 1, Issue 2, pp. 55-58, 2016.

nucleation sites, leading to larger grain size (spherical particles of uniform size ~ 50 nm) [12].

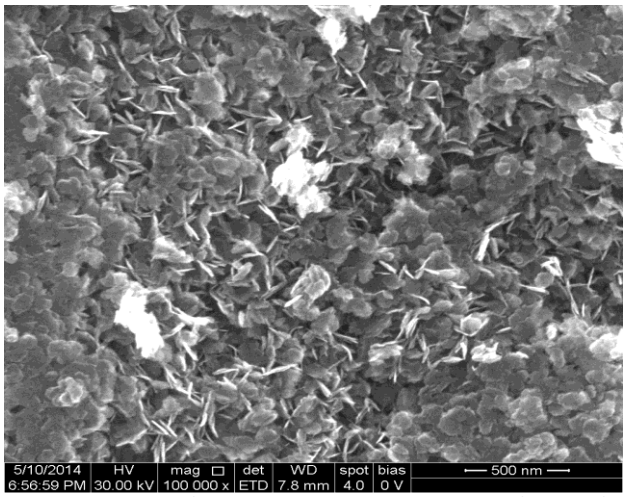

Fig. 4. FESEM image of pure NiO nanoparticles with a magnification of 500 nm

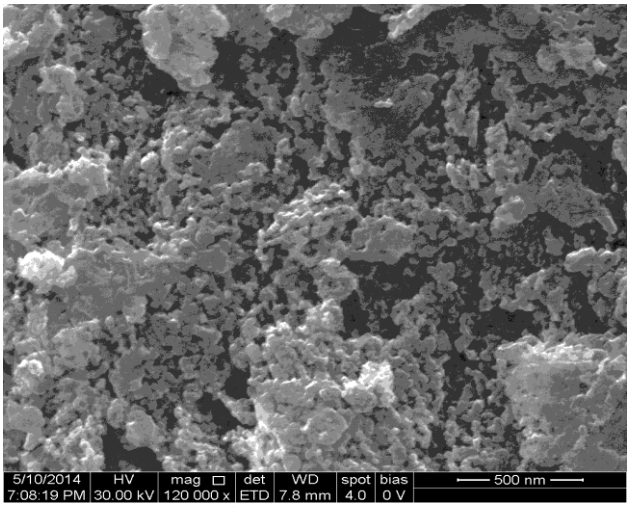

Fig. 5. FESEM image of 0.01 M Li doped NiO nanoparticles with a magnification of 500 nm

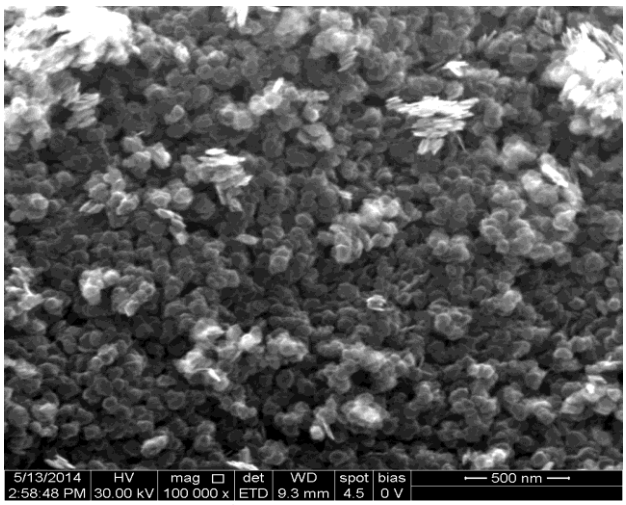

Fig. 6. FESEM image of 0.09 M Li doped NiO nanoparticles with a magnification of 500 nm

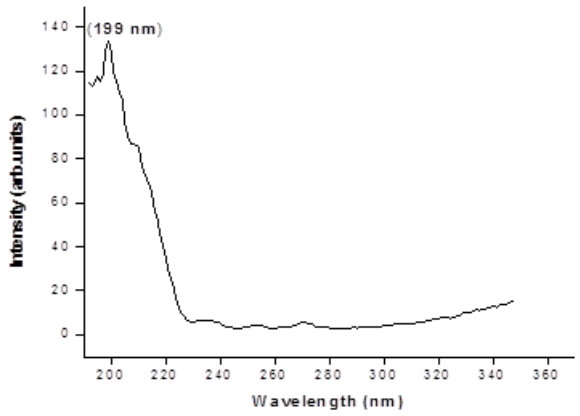

Fig. 7. PL emission spectrum of pure NiO nanoparticles

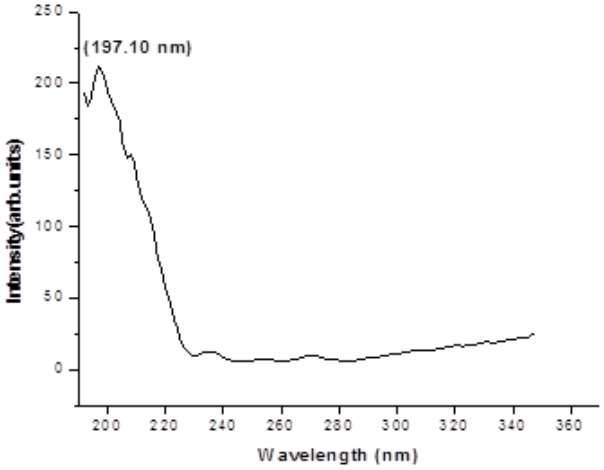

Fig. 8. PL emission spectrum of 0.01 M Li doped NiO nanoparticles

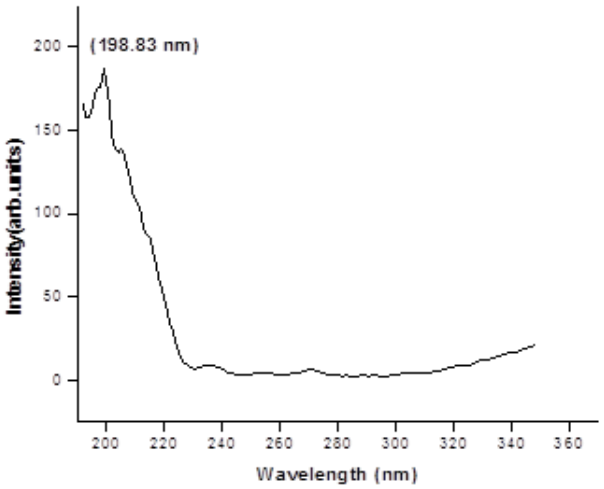

Fig. 9. PL emission spectrum of 0.09 M Li doped NiO nanoparticles

Figure 7 to figure 9 depicts the room temperature photoluminescence (PL) emission spectra for the pure and Li doped NiO nanoparticles. For all the three nanopowder

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samples, PL emission plots contain peaks centered around 198 nm under an excitation wavelength of 270 nm. The emission thus shows a blue shift indicating the nanosize of the synthesized particles.

IV. CONCLUSION

Pure and Li doped NiO nanoparticles are synthesized by a cost-effective sol-gel method. All the samples exhibit cubic structure. As the Li doping concentration increases, the crystallinity and average grain size of the samples increases and hence the dislocation density decreases. No impurity peaks are identified in the PXRD pattern. The FESEM images reveal the morphology of NiO nanoparticles in a regular uniform sized pattern as the lithium dopant increases. Photoluminescent emission spectra reveal the blue shift exhibited by the synthesized nanoparticles. Hence these Li doped NiO nanoparticles can be used for catalytic and gas sensor applications.

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