Synthesis, Structural and Optical Properties of Cr-Doped Nickel Oxide (NiO)

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Abstract: Cr doped nickel oxide (NiO) were successfully synthesized using a one-step solid state reaction method. The X-ray diffraction patterns analysis shown that all doped NiO powder samples were exhibited polycrystalline structures. When NiO doped with the different elements such as Cr then substantial modifications and anomalies were observed in NiO such as, morphology, thickness, lattice constant, stress/strain, crystallite size, and dislocation density. The doping in NiO also altered optical properties. Moreover, the characteristic deviations in the doped NiO powder have been thoroughly discussed.

Keywords: Solid state reaction, X-ray diffraction patterns, Polycrystalline, Powder morphology, Optical properties.

INTRODUCTION

In this era of fast reaction in development of instruments and electronics, Ni has become an interesting element. It’s oxidized form possessing semiconducting properties which is enabling several applications such as gas sensors, dyed sensitized photo cathodes and electrodes in alkaline batteries.

Nickel oxide (NiO) is a p-type metal oxide semiconductor with a wide band gap energy of 3.6–4 eV. Generally, NiO exhibits both rhombohedral and cubic structures. However, its lattice structure is dominated by the cubic structure \cite{1}. The p-type conductivity of NiO is attributed to the cation deficit or Ni vacancies in the lattice. Recently, this binary oxide has attracted much attention in many applications such as solar cells, batteries, sensors, energy storage, and memory devices \cite{2–7}. There are many techniques that have been applied to fabricate NiO either in powder structures or films, including spray pyrolysis, sputtering, hydrothermal, and solution-based methods \cite{8–12}. A doping process with metal elements has been regarded as one of effective approaches to modify the NiO properties. It has been reported that the doped NiO shows enhanced sensing performance and improved energy storage capacity \cite{13,14}. Therefore, the optimization of the doping process, including the selection of suitable dopant materials, is very crucial to improving the NiO properties. Recently, a few metal sources, which include lithium, indium, tin, manganese, iron, and cobalt, have been used as dopants in NiO \cite{15–18}. Each dopant alters the NiO characteristics when it is incorporated into the NiO lattice, and these characteristic variations are very useful for different kinds of applications. However, the characteristics of the doped NiO are also significantly influenced and controlled by the preparation methods and their corresponding parameters. In other words, NiO prepared by different methods but with similar dopants might exhibit different characteristics. Therefore, it is difficult to compare and evaluate the conclusive impact of the various dopants on the properties of NiO based on the reported works due to variances of the methods and parameters used to prepare the doped NiO. Each method might have different.
EXPERIMENTAL DETAILS

The pure and Cr doped Nickel oxide were synthesized by solid state reaction method. The initial precursor were high purity (MERCK) (99.9% pure) after this doping with Cr by the Cr₂O₃ and sintered at 750°C with the concentration 7.5%, 10% and 20% of Cr doping. Nickel Oxide and Chromium Oxide doped with molecular ratio according to calculation with different percentage and grinding for four to five hours.

The synthesized samples were characterized by XRD and UV-Vis. X-ray diffraction was conducted with the help of the Bruker D8 Advance X ray diffractometer with Cu Kα radiation (0.154 nm) in the angle range 20°-90°. In the UV measurements obtain the reflectance data from the Perkin Elmer USA model Lemda 950 with resolution 0.05nm.

RESULTS AND DISCUSSIONS

The crystalline structures of Ni₁₋ₓCrₓO with x=0.075, 0.1 and 0.2 are illustrated in Fig.1. As seen in XRD patterns, the diffraction peak displays only NiO cubic phase positioned at 2θ = 43.8° attributing to (200) orientation plane [12, 13]. From XRD patterns, it is indicated that the growth along the (200) plane tends to be the preferred orientation of these samples by solid state route. It is noticed that the diffraction peak intensity becomes weaker as Cr doping content increases, reflecting the deterioration in its crystallinity and the increase in disorder leading to partial amorphization of NiO with increasing Cr doping concentration [14]. It has been reported that the introduction of selective element with comparably close ionic radius to Ni²⁺ such as Li¹⁺ [8], Al³⁺ [10], Cu²⁺ [15], and W⁶⁺ result in the significant decreasing in crystallinity and domination of amorphous phase of NiO. The incorporation of Zn additive into NiO could deter the crystallization because of the lattice distortion [16], which could be beneficial for the different performance of NiO compound. Doped NiO samples exhibit polycrystalline structures, which belong to the space group of Fm3m face-centered cubic (FCC) NiO phase (JCPDS# 47–1049). The XRD pattern reveals that the NiO sample has four diffraction peaks at 37.8°, 43.8°, 63.3°, and 75.8°, corresponding to (111), (200), (220), and (311) orientations, respectively. The pristine sample shows sharp and clear diffraction peaks demonstrating a good crystalline quality. However, the intensities of these peaks was reduced significantly when the NiO samples were doped with Cr sources. The shift of the Bragg angles θ, to higher-angles, was observed for the XRD peaks with the addition of dopants. These angle shifts show that interactions take place between the dopants and Ni in the lattice due to their electronegativity differences (Cr: 1.66 Pauling, Ni: 1.91 Pauling); this corroborates the integration of the dopants into the NiO lattice. This positive shift of diffraction peaks for the doped NiO samples also denotes the change of lattice parameters to lower values, revealing the fractional assimilation of dopant ions into the NiO lattice. For the doped samples, the FWHM of the XRD peaks were also broadened, which is due to the substitution of randomly localized dopant ions at the Ni²⁺ sites in the NiO lattice. These dopant ions interrupt the equilibrium of the system and transform the properties of NiO. These results indicate that the crystallinity of the sample reduces after the doping process. This decline in crystallinity with addition of dopants is in agreement with the knowledge that the crystal growth could be inhibited due to the integration of dopants into the NiO lattice [19]. Scherrer’s formula was applied to estimate the crystallite size D from the (111) peak as shown by the following equation [20, 21]:

\[
D = \frac{\kappa \lambda}{\beta \cos \theta}
\]

(1)

Where K represents a constant, given as 0.9, while λ is the XRD’s X-ray wavelength (i.e., 1.5418 Å).

Meanwhile, θ denotes the diffraction angle and β refers to full-width at the half maximum (FWHM), which correlates with the diffraction broadening due to the dimensions of the crystallite. The crystallite sizes at different plane orientations, namely (200), (220), and (311), were also estimated based on the Scherrer formula

\[
d = \frac{n \lambda}{2 \sin \theta}
\]

(2)

where h, k, and l denote the Miller indices of the (111) planes, while λ represents the X-ray wavelength. In this equation, θ is the diffraction angle of (111) plane and n refers to the value for order of diffraction, which is normally given as 1. From the values obtained, it can be seen that lattice shrinkage is observed for all samples as compared to that of the bulk NiO (4.1771 Å), which could be attributed to the Ni vacancies and dopant integration into the NiO lattice [24]. The optical reflectance spectra of Cr doped NiO are shown in Fig.2,3,4. The spectra indicate that the samples have reflectance in the visible region, with average values of 26%, 40%, 73% and 91% for Cr doped NiO,
respectively. However, the spectra show that all samples have an onset of fundamental absorption in the UV region at a wavelength below 400 nm. The modifications in the fundamental absorption after the doping process are an indication of dopant incorporation in the NiO lattice, which changes the gap states. For a direct band gap semiconductor material, the parabolic band gap energy $E_g$ and absorption coefficient $\alpha$, can be linked by the following equation:

$$a\nu = A(\hbar\nu - E_g)^{1/2}$$

(3)

where $A$ denotes a constant, while $\hbar\nu$ represents the photon energy. The band gap energy of the samples can be estimated by plotting $(a\nu)^2$ against the $\hbar\nu$, where the extrapolated linear line of this plot at the $\hbar\nu$ axis gives the band gap of the samples. The estimated $E_g$ values from the Tauc plot in Fig.2,3,4 for Cr doped NiO samples are has been shown. According to this result, the band gap values of the sample are $Cr7.5 < Cr10 < Cr20$. This ordering also reflects the lattice contraction as discussed in the XRD analysis. Ghosh et al. reported that the contaction of the lattice causes the band gap broadening of the samples [30]. The contraction of the lattice size provides a broader band gap because of the augmented repulsion between the Ni 3d and O 2p orbitals. According to Dewan et al., the band gap energy of the doped NiO film can also be influenced by oxygen vacancy defects [26]. The oxygen vacancy defects could form extra defect states in the forbidden region between valence band and conduction band, which may reduce the band gap of sample. The shift of the band gap energy may be affected by the delocalization state at the edge of the conduction band, which facilitates shallow traps or deep traps in the electronic band. Carbone et al. reported that the band gap energy of the samples is also influenced by the thinness and porosity of the samples [31]. These conditions provide defect states at the internal hole boundaries, which affects the band gap. The thin and

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<th>FIGURE 1. XRD spectrum of Cr doped Nickel Oxide (NiO)</th>
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dense samples tend to have larger band gaps. In their study, Akaltun et al. reported that thin NiO tends to exhibit larger bandgaps due to changes in crystal structure, morphology, atomic distance, grain size, and structural defects in the films [32]. The refractive index $n$ values for the $Cr7.5$, $Cr10$ and $Cr20$ samples were estimated using the Moss relation, which has a direct correlation with the optical band gap energy. The formula is given below [32–34]:

$$n = \left(\frac{k}{E_g}\right)^{1/4}$$

(4)

Here, $k$ denotes a constant with a given value of 108 eV. The refractive index $n$ can also be estimated using a different equation suggested by Herve and Vandamme, as shown below [49–51]:

$$n = \sqrt{1 + \left(\frac{A}{B+E_g}\right)^2}$$

(5)

where $A$ is the hydrogen ionization energy with a value of 13.6 eV, while $B$ is a constant related to UV resonance energy and band gap energy difference with a value of 3.4 eV.
CONCLUSION

In conclusion, Cr doped nickel oxide of various compositions were prepared by using a simple and inexpensive solid state reaction route. The XRD study shows that all the doped nickel oxide samples were crystallize in cubic phase and crystallinity changes as the doping of Cr increases morphologies with small doped samples structures and reduced thicknesses. The crystalline properties of the doped samples also deteriorated, which signifies the incorporation of dopants into the NiO lattice. The results also reveal the formation of high purity Cr-NiO samples. The UV-Vis reveals the change of energy band gap as the doping percentage increases. As the doping percentage of Cr increases the optical band gap also increases. Where the increase of these characteristics was most pronounced for the Cr20-doped, followed by the doped, Cr10-doped, and Cr7.5-doped samples. These characteristic deviations of the Cr doped NiO very useful for different kinds of applications.

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REFERENCES


FIGURE 3. Tauc Plot for Energy band gap of 10% Cr doped Nickle Oxide (NiO)

FIGURE 4. Tauc Plot for Energy band gap of 20% Cr doped Nickle Oxide (NiO)