Structure and optical properties of nano Ni$_x$ Cd$_{1-x}$ Fe$_2$O$_4$ doped with optical dyes

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Abstract. Ni$_x$Cd$_{1-x}$Fe$_2$O$_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) nanoferrite powder were synthesized using flash auto combustion method. The studied powder was characterized by X-ray diffraction (XRD), which was used to determine the structural properties. The effect of addition dyes (perylene dye and thiophene dye) on the optical properties of Nickel Cadmium ferrite has been investigated. The optical study UV–Visible is used to calculate the band gap energies. From Tauc’s plot, it can be seen that the band gap energy of the samples is decreasing with increase in nickel content for both dyes, indicating the enhancement of the optical of ferrite.

1. Introduction

In the recent years, Ferrites have been investigated by many researchers because of their unique dielectric, magnetic and optical properties. These ferrites are very important group of magnetic materials due to their extensive use in a wide range of applications from low to high permeability devices including electronics, magnetic drug delivery, microwave devices, ferrofluid and high density information storage devices [1].

Ferrite based materials can be prepared using different methods viz. co-precipitation [2], sol–gel [3], combustion [4] and hydrothermal synthesis [5]. The flash method is among the important method for preparing of different ferrites [6].

Liquid solutions of organic laser dye molecules have been widely used as good laser gain media from the near UV to the near IR region of the spectrum [7]. There are several disadvantages in using liquid dye lasers like poor thermal stability of dye solutions, requirement of large volume of solutions and need of significant maintenance, etc. [8]. These difficulties can be overcome by doping stable laser dye molecules into restricted host matrices like polymers, silica gels, xerogels and sol–gel glasses [9-13]. Solid-state dye laser presents some advantages, e.g. they do not contain volatile solvents, they are non-flammable, nontoxic, and compact in size and mechanically and thermally more stable [7-8].

Recently, a lot of work is devoted to implement laser dyes in solid-state as the practical alternative to the counterpart liquid, dye lasers due to their compactness, low cost of fabrication ease and safety in handling and operation. Also, to avoid lack of toxicity, flammability, flow fluctuations, and solvent evaporation problems [13-15]. Several solid-state dye lasers (SSDL) restricted matrices have been widely reported. They played an important role in urology, cardiology and dermatology [16].
2. Preparation Techniques
Ni$_x$Cd$_{1-x}$Fe$_2$O$_4$ synthesis using flash method where $x = (0, 0.1, 0.2, 0.3, 0.4, 0.5)$ Cd nitrate (Cd(NO$_3$)$_2$.6H$_2$O), and ferric (Fe(NO$_3$)$_3$.9H$_2$O), and urea (CO(NH$_2$)$_2$) were used as starting materials. The metal nitrates were mixed with the urea by using glass rod. The mixing was heated at 80°C with constant stirring using hot plate. The mixing became viscous and finally forming brown powder.

The preparation of optical part was made by using pure ferrite and ferrite 3, 4:9, 10-pyrenetetracarboxylic anhydride dye (perylene dye) and 2.5/dis (5-tert-duty/-2-denzoxazoly/ thiophene dye) (BBOT) nanocomposite with different ratio of dyes.

Also, we add 10 ml methanol to 0.03 gm 3, 4:9, 10-pyrenetetracarboxylic anhydride dye and 0.03 gm 2.5/dis (5-tert-duty/-2-denzoxazoly/)thiophene dye. To prepare the studied sample for optical properties we use 0.2 gm of ferrite to be suspended in 25 ml deionized water. 1ml of dye in methanol was added to the suspension of ferrite in deionized water. The solution of dye was added to all ferrite sample Ni$_x$Cd$_{1-x}$Fe$_2$O$_4$, where $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5.

3. Results and discussion.

3.1. The XRD.
The XRD pattern of Nickel ferrite polycrystalline and Nickel Cadmium ferrite are shown in Figure 1. The diffraction of peaks can be indexed in the viewer cubic spinel [17]. The average crystallite size was calculated between the FWHM of the main peak (311) using Scherer equation [18]:

$$d = \frac{0.89\lambda}{\beta \cos{\theta}}$$  \hspace{1cm} (1)

Where $\lambda$ is the wave length of the X-ray for Cu-Kα radiation source ($\lambda = 1.5405$ Å), $\theta$ is the Bragg angle (which is ranged from 1-40 degree), $\beta$ is the full width at half maximum (FWHM) corresponding to sharp intense peak (in radian).

![Figure 1. The XRD of Nickel ferrite polycrystalline and Nickel Cadmium ferrite.](image_url)
The particle size is much larger than the crystallite size calculated by Scherrer equation indicating that the particles are consisting of nickel cadmium crystallites. The X-Ray density and porosity was calculated using relation [18]:

$$D_x = \frac{8M}{Na^3},$$

(2)

where M is the molecular weight, N is Avogadro’s number and a is the lattice constant.

$$P = 1 - \frac{D}{D_x},$$

(3)

where P is the porosity, D is the bulk density and D_x is the theoretical density.

The diffraction pattern with different particle size thereby confirming by the chemical reaction was completed without any impurity phases. The decrease of lattice parameter by increasing nickel content is due to the smaller ionic radius of nickel compared with cadmium ion (0.84A°) where nickel (0.69A°) which leads to lattice is shrinking [19].

The smaller atomic weight of nickel compared with cadmium leads to the decrease of density, leading to the increase of porosity as given in Table 1 and figure 2.

| X  | Lattice parameter a (Å) | Crystallite size t (nm) | Density D_x (gm/cm^3) | Bulk density D (gm/cm^3) | Porosity P  |
|----|------------------------|-------------------------|-----------------------|-------------------------|-------------|
| 0.0 | 8.58                   | 23.09                   | 6.06                  | 2.39                    | 0.606       |
| 0.1 | 8.57                   | 13.96                   | 5.97                  | 2.46                    | 0.588       |
| 0.2 | 8.56                   | 16.05                   | 5.87                  | 2.46                    | 0.581       |
| 0.3 | 8.55                   | 15.09                   | 5.77                  | 2.37                    | 0.589       |
| 0.4 | 8.57                   | 14.55                   | 5.62                  | 2.27                    | 0.596       |
| 0.5 | 8.52                   | 9.37                    | 5.61                  | 2.29                    | 0.591       |
The single phase formed in XRD pattern indicates the solubility of the constituent into their respective lattice size. The decrease of lattice constant is observed with increasing nickel content. The decrease of lattice constant is expected in view of the fact that the ionic radius of substitute nickel ion (0.69Å) is smaller than cadmium ion (0.84Å) [19].

In the present investigation the mechanism of replacing cadmium by nickel ions can be understood in the following manner as cadmium prefer to occupy tetrahedral site, the vacancy created by the removal of cadmium by nickel ions at octahedral site will be filled by the migration of iron ions from tetrahedral to octahedral. The cation distribution is now modified as: (Cd_{1-x}Fe_x) (Ni_xFe_{2-x})O_4

The decrease of lattice parameter with increases in nickel content suggest the modification of unit cell and consequently noticeable variations in the u-parameter , in tetrahedral and octahedral bond lengths and in average cation radius at A and B-sites can be anticipated. The variations of these parameters with nickel content in table 2.
Table 2. The variation of Ni content with ionic radii, theoretical lattice parameter, experimental lattice parameter and oxygen positional parameter.

| x-value | $r_A (\text{Å})$ | $r_B (\text{Å})$ | $a_{th} (\text{Å}^3)$ | $a_{exp} (\text{Å}^3)$ | $u (\text{Å}^3)$ |
|---------|------------------|------------------|------------------------|------------------------|------------------|
| 0       | 0.84             | 0.645            | 8.56                   | 8.58                   | 0.395            |
| 0.1     | 0.81             | 0.647            | 8.52                   | 8.57                   | 0.393            |
| 0.2     | 0.77             | 0.649            | 8.47                   | 8.56                   | 0.391            |
| 0.3     | 0.73             | 0.652            | 8.42                   | 8.55                   | 0.388            |
| 0.4     | 0.7              | 0.654            | 8.37                   | 8.57                   | 0.386            |
| 0.5     | 0.67             | 0.656            | 8.32                   | 8.52                   | 0.385            |

The average cation radius of A and B sites as function of nickel content has been calculated from the following equations [19]:

$$r_A = (1 - x)r_{Cd(A)} + xr_{Fe(A)}$$ \hspace{1cm} (4)

$$r_B = \left(\frac{1}{2}\right)\left[xr_{Ni(B)} + (2 - X) r_{Fe(B)}\right]$$ \hspace{1cm} (5)

The ionic radii values involved in the calculation are: Cd$^{2+}$(0.84\text{Å}), Ni$^{2+}$ (0.69\text{Å}) and Fe$^{3+}$ at A-site = (0.49\text{Å}), B-site = (0.645\text{Å}). The oxygen positional parameter ($u$) as a function of nickel concentration can be calculated using the expression [19]:

$$r_A = (u - 0.25)a\sqrt{3} - R_O$$ \hspace{1cm} (6)

Where $u$ is the oxygen positional parameter, $a$ is the experimental lattice constant and $R_O$ is the radius of the oxygen ion. The lattice constants ($a_{th}$) has also been calculated from the relation [19]:

$$a_{th} = \frac{8}{3\sqrt{3}}\left[(r_A + R_O) + \sqrt{3}(r_B + R_O)\right]$$ \hspace{1cm} (7)

The very close agreement between the experimental and calculated lattice parameter from cation distribution confirms the occupancy of cadmium ions of A-site, also the theoretical values of the lattice constant are slightly higher in comparison with that experimental values. This attributed to the fraction of Fe$^{2+}$ which have higher ionic radius than Fe$^{3+}$.

3.2. Optical properties of ferrite dye laser nano composite.

Absorption of light energy in UV/V is regions by pure ferrite and ferrite 3, 4:9, 10-perylenetetracarboxylic anhydride dye (perylene dye) and 2.5/dis (5-tert-duty/-2-denzoxazoly/ thiophene dye) (BBOT) nano composite with different ratio of dyes.

Firstly, we add 10 ml methanol to 0.03 gm 3, 4:9, 10-perylenetetracarboxylic anhydride dye and 0.03 gm 2.5/dis(5-tert-duty/-2-denzoxazoly/thiophene dye). To prepare the studied sample for optical properties we use 0.2 gm of ferrite to be suspended in 25 ml deionized water. In this case 1ml of dye in methanol is added to the suspension of ferrite in deionized water.
The solution of dye is added to all ferrite sample $\text{Ni}_x\text{Cd}_{1-x}\text{Fe}_2\text{O}_4$, where $x=0$, 0.1, 0.2, 0.3, 0.4 and 0.5 and the UV absorption spectra of the samples are shown in figure 3 and figure 4.

![Figure 3. UV of ferrite BBOT dye composite.](image1)

![Figure 4. UV of ferrite perylene dye composite.](image2)

The UV spectra of pure ferrite samples did not show any absorption peak due to the opaque character and the poor optical properties of ferrite except the sample $x=0.4$ and $x=0.5$ have peak around 1000nm.

The composite sample implies transition of electron in $\pi,\sigma$ and in orbital from one energy state to another higher energy state. The UV spectrophotometer has become fitting device for inspecting these electronic transitions and calculates the optical energy gap. The main absorption edge for BBOT was found to be shifted to longer wavelength by increasing nickel content in the ferrite samples. These shift
indicating the complexation between the ferrite and dyes which its UV absorption spectra is show in Figure 3. This shift in absorption edge reflects the variation in the optical energy gap.

The sample ferrite perylene composite has absorption peak near 600nm. This peak shifted to longer wavelength by increasing nickel content in the ferrite samples. These shift indicating the complexation between the ferrite and dyes which its UV absorption spectra is show in figure 4.

Determination of optical energy gap using Davis and Mott formula: The optical $E_g$ for indirect transition for all studied samples were examined using the equation [20]:

$$a h\nu = c (h\nu - E_g)^n,$$  \hspace{1cm} (8)

where: $\alpha$ is the absorption coefficient $= \frac{2.34}{X}$, A is the absorption, X is the thickness, and n is the power that can take values 1/2 or 1 depending on the nature of electron transitions.

The values of optical energy gap can be calculated from extrapolated linear section of photon energy $h\nu$ versus $(\alpha h\nu)^{1/2}$[21]. The calculated values were recorded in table 3 and plotted versus nickel concentration to trace the effect of nickel concentration in ferrite in the optical characteristic in ferrite show that $E_g$ decrease with increase of nickel content as shown in figure 5.

**Table 3.** Optical energy gap for different complex samples as a function of Ni content.

| Nickel content | Davis and Mott formula | Tauc’s equation |
|----------------|------------------------|-----------------|
|                | perylene dye | optical $E_g$ (eV) | BBOT dye | optical $E_g$ (eV) | Perylene dye | optical $E_g$ (eV) | BBOT dye |
| 0              | 2.16        | 3.61              | 3.03      | 3.47              |
| 0.1            | 2.12        | 3.52              | 3.01      | 3.46              |
| 0.2            | 1.68        | 3.49              | 2.99      | 3.44              |
| 0.3            | 1.54        | 3.46              | 2.96      | 3.36              |
| 0.4            | 1.47        | 3.40              | 2.95      | 3.34              |
| 0.5            | 1.24        | 3.37              | 2.94      | 3.14              |

The values of optical energy gap were calculated, considering the perylene dye as indirect semiconductor material and BBOT dye as direct semiconductor material.

![Figure 5. Optical energy gap for different complex samples as function of Ni content using Davis and Mott.](image-url)
Experimental data indicates a present of charge transfer complexes between ferrite and dye laser arising from the disordering and defect formation result from adding the dye to ferrite. Such defects result in overlap in the recolised state and responsible for the decrease of optical energy gap for the ferrite perylene composite as shown in figure 7 and ferrite BBOT composite as shown in figure 8.
Figure 7. Optical activation energy gap for ferrite–perylene composite.
Determination of optical energy gap using Tauc’s expression \((E_g)\) Tauc’s expression\([22]\):

\[
E_g = \frac{h\nu}{\lambda_g},
\]

(9)

where \(\lambda_g\) is Tauc’s wavelength. The energy gap decrease by increasing nickel content as shown in Table 3 and Figure 6.

4. Conclusion.
1) All X-ray diffraction patters showed a single phase spinel structure and the lattice constant has been observed to decrease with increasing nickel content.
2) The smaller atomic weight of nickel compared with cadmium leads to the decrease of density and increase of porosity.
3) The mechanism of replacing cadmium by nickel ions can be understood in the following manner as cadmium prefer to occupy tetrahedral site, the vacancy created by the removal of cadmium by nickel ions at octahedral site suggest the modification of unit cell and consequently noticeable variations in the oxygen positional parameter, tetrahedral and octahedral bond lengths \((\text{Fe}^{2+}\text{O}^{2-})\).
4) For optical measurements the dyes were dissolved in methanol and a suspension of ferrite powder in the dye solution was used to measure the optical properties using UV-visible spectra. The doping of dyes in ferrite decrease the band gap energy and enhancing the optical properties of ferrite.

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