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Fe Doping Induced Shrinking of Band Gap of NiO Nanoparticles

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Abstract We synthesized $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles by chemical co-precipitation method and studied the effect of Fe on the optical properties of NiO. UV-visible characterization of these samples indicated that the optical band gap of NiO decreased from 3.65 to 3.43 eV when the doping concentration increased from x = 0 to x = 0.02. Since NiO is a p-type material and the holes are expected to populate at the top of the valence band due to Fe doping which can cause the band gap shrinkage as is seen in our case. The refractive index and electron polarizability with Fe doping concentration in NiO have been determined from the optical band gap. Both refractive index and electron polarizability follow opposite trend as compared to the energy gap as a function of Fe doping concentration.

Keywords Nanoparticle, NiO, Doping, Co-precipitation method, UV-Visible Spectroscopy

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1. Introduction

Nanoscale transition metal oxides (TMOs) attracted much research attention due to their potential applications. Among the different well studied TMOs, NiO with rock salt structure is an attractive material well known for its chemical stability. NiO has shown its potentiality in wide range of technological applications such as gas sensor [1], p-type transparent conductor [2], electrochromic material for smart windows [3], resistive random access memory [4] etc. Doping with TM could change properties of NiO which can be useful for different applications. NiO nanoparticles exhibit room temperature ferromagnetism at the expense of parent antiferromagnetic property when doped with Fe [5-8]. Mn doping led to appearance of superparamagnetism [9] whereas Co doping retains the parent antiferromagnetic property in NiO [10]. Even slightly changing the synthesis conditions led to the appearance of superparamagnetic properties in place of ferromagnetism in Fe doped NiO [11].

Change in optical band gap of NiO with doping has been reported [12-14]. Changing the band gap will affect different properties of material and these materials are necessary to build many technologically important devices [15].

In the present work, $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles synthesized by chemical co-precipitation method and the effect of Fe on the band gap of NiO is studied.

2. Experimental Methods

The $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles synthesized by chemical co-precipitation method as described elsewhere [8]. The evolution of band gap, refractive index and electron polarizability in $Ni_{1-x}Fe_xO$ samples were characterized by diffuse reflectance spectroscopy using an UV-Visible spectrophotometer (Simadzu, UV-2450) having an integrating sphere assembly.

3. Results and Discussion

Figure 1 shows the variation of absorption coefficient (α) with photon energy ($h\nu$) for $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles synthesized by chemical co-precipitation method. As indicated from the Fig. 1, the absorption intensity for all samples increased with increasing energy due to nanocrystalline nature of the material [16]. The evolution of optical band gap (E_g) of NiO with Fe doping can be extracted from the α using the following relation [17]:

$$\alpha = \frac{B(h\nu - E_g)^m}{h\nu} \tag{1}$$

where B is a materials dependent constant. The constant m takes the values of 1/2, 3/2, 2 or 3 respectively [18] for direct allowed, direct forbidden, indirect allowed or indirect forbidden transition. One can determine the value of E_g for a given material by extrapolating the linear portion of the $(\alpha h\nu)^{\frac{1}{m}}$ vs. $h\nu$ plot to $\alpha = 0$. The linear relation observed

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for $(\alpha h\nu)^2$ vs. $h\nu$ plot (Fig. 2) indicated that the $Ni_{1-x}Fe_xO$ nanoparticles exhibit direct allowed transition as was seen for NiO nanostructures [19].

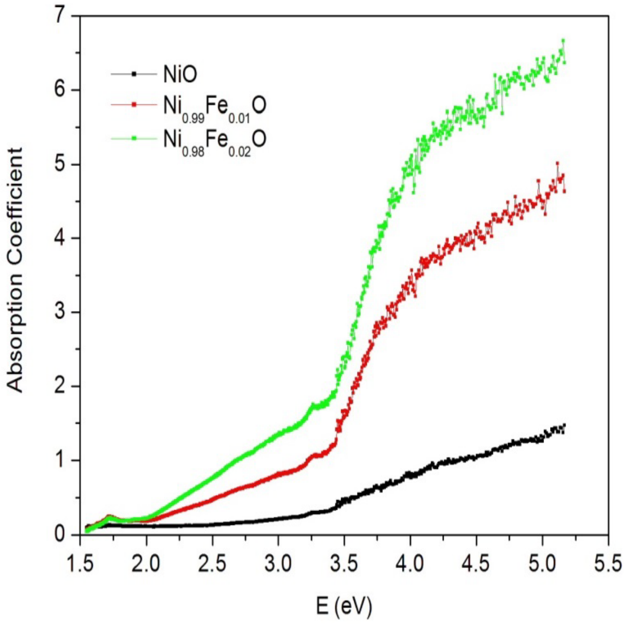

Figure 1. Variation of absorption coefficient (α) with photon energy ($h\nu$) for $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles

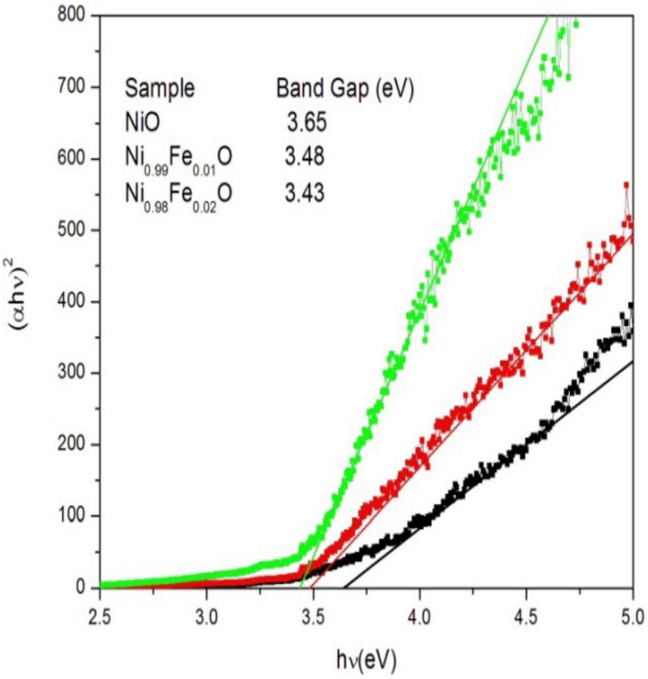

Figure 2. Variation of $(\alpha h\nu)^2$ vs. photon energy, $h\nu$ for $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles

The value of E_g of NiO decreased from 3.65 to 3.43 eV with increasing doping concentration from x = 0 to x = 0.02 (Fig. 3). It is well known that the carriers introduced with dopants which occupy the energy states near the band edges of the host semiconductor in a doped semiconductor [12]. NiO is a p-type material and the holes are expected to generate at the top of the valence band due to Fe doping. When Fe^{3+} occupies Ni site, two such Fe ions can lead to a vacancy at Ni site and each Fe substitution at Ni site led to a hole in Fe doped NiO matrix [5]. These holes cause the bandgap shrinkage [20] as is seen in our case. Similar observation has been reported for Al doped NiO [12]. These holes not only affects the optical band gap but also causes the emergence of ferromagnetic ordering at the expense of antiferromagnetic ordering of host NiO and possibly due to the double exchange interaction between Fe ions and free charge carriers [5]. The appearance of room temperature ferromagnetism in this system [5-8] could useful for the possible application of this material in spintronic devices.

Refractive index (n) of $Ni_{1-x}Fe_xO$ nanoparticles can be calculated from the E_g as per the following relation [21]:

$$n = KE_g^C \tag{2}$$

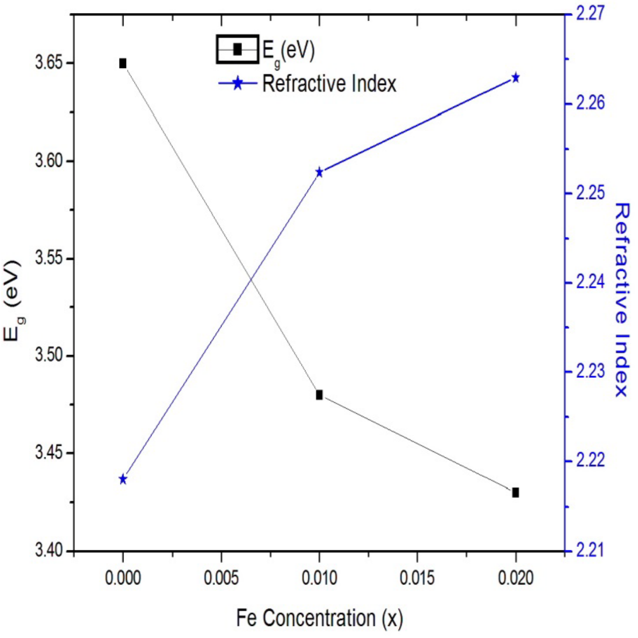

Figure 3. Variation of E_g and refractive index (n) in $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles

where K = 3.3668 and C = -0.32234. The variation of 'n' with Fe doping concentration in NiO is shown in Figure 3. These values of n match closely with that of visible light transparent NiO thin film [22]. The 'n' is related to the electron polarizability (α') of ions and local field inside the material. The values of classical electron polarizability ($\alpha'_{classical}$) and α' from E_g for Ni1-xFexO nanoparticles can be calculated as per the following relations [23, 24]:

$$\alpha'_{classical} = \frac{(n^2-1)}{(n^2+2)}\frac{M}{\rho}\times 0.395\times 10^{-24}\ \text{cm}^3 \tag{3}$$

and

$$\alpha' = \left[\frac{12.41-3\sqrt{E_g-0.365}}{12.41}\right]\frac{M}{\rho}\times 0.395\times 10^{-24}\ \text{cm}^3 \tag{4}$$

where M and ρ are molecular weight (g/mol) and density (g/cm^3) of the substances, respectively. Figure 4 shows the evolution of $\alpha'_{classical}$ and α' with different Fe doping concentration in NiO.

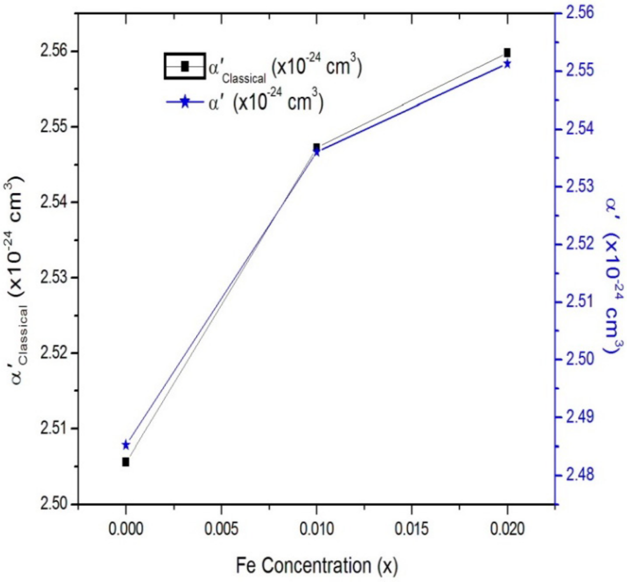

Figure 4. Variation of $\alpha'_{classical}$ and α' in $Ni_{1-x}Fe_xO$ (x = 0, 0.01 and 0.02) nanoparticles

4. Conclusions

The UV-visible spectroscopic characterization of $Ni_{1-x}Fe_xO$ nanoparticles showed Fe doping causes the shrinking of optical band gap of NiO. The refractive indices extracted using E_g values are enhanced with Fe doping in NiO nanoparticles. The values indicated that the Fe doped NiO nanoparticles are transparent to visible light. Our study thus indicates that the shrinking of band gap in $Ni_{1-x}Fe_xO$ samples could be useful for optical device applications.

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