Band gaps of nanocomposites

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Nanocomposites of Ni-Zn with copolymer matrix of aniline formaldehyde in presence of varying concentrations of zinc ions have been studied at room temperature and normal pressure. The absorption spectra of these materials are recorded by a Hitachi spectro-photometer, model U-3400, in the wavelength range 850-410 nm. From the analysis of absorption spectra, nanocomposites copolymer of aniline formaldehyde Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$) have been found to have direct band gaps ranging from $1.54$ eV to $1.88$ eV. Sudden increase in the band gap of these composites in the vicinity of composition from $x = 0.2$ to $x = 0.4$ has been explained on the basis of structural change at those concentrations of Zn.

1 Introduction

Materials with nanoscale microstructure i.e. nanoparticle give rise to some unique properties e.g. electrical, magnetic and optical properties. Further, high surface area of nanomaterials enhances their absorption properties. The nanomaterials can be polycrystalline or amorphous in nature and may belong to inorganic, organic or combination of both classes of material. The nanocomposites is one of the very important class of nanomaterials. Some of the important applications of magnetic nanocomposites are magnetic refrigeration at high temperature, high-density information storage, colour imaging, ferrofluids, medical diagnosis, electromagnetic wave absorption etc. In the present study the absorption spectra of nanocomposites materials is recorded by a Hitachi spectro-photometer, model U-3400, in the wavelength range 850-410 nm and the band gap determinations have been made.

2 Experimental Details

Nanocomposites of Ni-Zn ferrite in a copolymer matrix of aniline-formaldehyde were synthesized at room temperature by using a novel chemical method reported elsewhere. The nanocomposites of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrites with $x = 0.0, 0.2, 0.4, 0.6$ and $0.8$ were synthesized in a copolymer matrix (containing three different monomers) of aniline-formaldehyde. As a typical preparation, sample S1 ($x = 0$) was synthesized by treating the aqueous solution of aniline (0.10 mole), hydrochloric acid (0.12 mole), formaldehyde (0.10 mole) and nickel (0.189 mole) taken according to the stoichiometry. The resulting solution was stirred thoroughly and added to 10% solution of alkali. The precipitated composite was washed repeatedly with the distilled water till the filtrate was free of alkali (pH 7.5) and then dried in air. Similarly, the samples S2-S5 ($x = 0.2, 0.4, 0.6$ and $0.8$) were synthesized using the same procedure by varying the quantities of nickel and zinc according to the stoichiometry.

3 Characterization of Sample

Absorption spectra of this materials is taken at room temperature with the help of Hitachi spectro-photometer, model U-3400. Its wavelength range is 187-2600 nm. The lead sulphide detector (PbS) is used for the detection of infrared rays. The visible wavelength light source is long life WL lamp. Energy band gap ($E_g$) of materials is related to absorption coefficient $\alpha$ as:

$$\alpha h\nu = A (h\nu - E_g)^n$$

where $A$ is a constant, $h\nu$ is the photon energy, $E_g$ the band gap and $n$ is an index which assumes the values $1/2, 3/2, 2, 3$ depending on the nature of the electronic transition responsible for the absorption. $n = 1/2$ is taken for an allowed direct transition. Therefore, by plotting a graph between $(\alpha h\nu)^2$ and $h\nu$, a straight line is obtained which gives the value of the direct band gap.

4 Results and Discussion

Absorption spectra of nanocomposites of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (with $x = 0.0, 0.2$) is shown in Fig. 1.
Fig. 1 — Absorbance versus wavelength for composition (●) Ni$_{1.0}$Zn$_{0.0}$Fe$_2$O$_4$ and (▲) Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$

Fig. 2 — Absorbance versus wavelength for composition (●) Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$, (▲) Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$, and (■) Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$

whereas the recorded absorption spectra for x = 0.4, 0.6 and 0.8 is shown in Fig. 2. It is observed from Figs 1 and 2 that, absorption decreases with the increase in wavelength. This decrease in the

Fig. 3 — $(ahv)^2$ versus photon energy for composition (●) Ni$_{1.0}$Zn$_{0.0}$Fe$_2$O$_4$

Fig. 4 — $(ahv)^2$ versus photon energy for composition (●) Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$.
absorption indicates the presence of optical band gap in these composites. Tauc relation as given in Eq. (1) is used for the determination of direct band gap in the nanocomposites of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$. Graphs between $(a(hv))^2$ versus $(hv)$ have been plotted in Figs 3-5, respectively. The extrapolation of straight line to $(a(hv))^2 = 0$ gives the value of direct band gap. From these graphs, the value of optical band gap of sample S1 (composite of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ with $x = 0.0$), S3 (with $x = 0.4$) and S5 (with $x = 0.8$) comes out to be 1.54 eV, 1.78 eV and 1.88 eV, respectively. For samples S2 (with $x = 0.2$) and S4 (with $x = 0.6$) the values of optical band gap are 1.56 eV and 1.82 eV. So, obtained values of optical band gap have been plotted in Fig. 6 for different compositions. It can be observed from Fig. 6 that, optical band gap increases sharply after $x = 0.2$ with the increase of Zn concentration in the nanocomposites of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$. This might be due to the fact that zinc additive in increasing concentration produces some kind of structural change for concentration between $x = 0.2$ and $x = 0.4$ of Zn in the nanocomposite. Also, there seems to be some possibility of phase transformation for these compositions, which will depend upon the fact that how actually zinc replaces nickel in the composite and enters into the matrix of aniline formaldehyde.

5 Conclusions

Nanocomposites of aniline formaldehyde have been found to have direct band gap which increases with the concentration of zinc in the composite.

Sudden increase of band gap between $x = 0.2$ and $x = 0.4$ indicates a phase transformation due to some kind of structural change in the vicinity of these compositions.

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References