Bull. Mater. Sci., Vol. 26, No. 4, June 2003, pp. 387–389. © Indian Academy of Sciences.

Band gap determination of Ni–Zn ferrites

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MS received 22 January 2003; revised 9 April 2003

Abstract. Nanocomposites of Ni–Zn with copolymer matrix of aniline and formaldehyde in presence of varying concentrations of zinc ions have been studied at room temperature and normal pressure. The energy band gap of these materials are determined by reflection spectra in the wavelength range 400–850 nm by spectrophotometer at room temperature. From the analysis of reflection spectra, nanocomposites of copolymer of aniline and formaldehyde with $Ni_{1-x}Zn_xFe_2O_4$ (x = 0·0, 0·2, 0·4, 0·6, 0·8 and 1·0) have been found to have direct band gaps ranging from 1·50–1·66 eV.

Keywords. Nanocomposite; optical properties; reflection spectra.

1. Introduction

In the past few years nanocomposites have become one of the most extensively studied materials all over the world as they possess several applications such as magnetic recording materials, sensors etc (Anderson *et al* 1980). The nanomaterials can be polycrystalline in nature and may belong to inorganic, organic or a combination of both classes of materials (Vadera *et al* 1997; Mathur *et al* 1999). Moreover, nanocomposite materials composed of oxides and conducting polymers have brought out more fields of applications such as smart windows, magnetic refrigeration at high temperature, high-density information storage, colour imaging, ferrofluids, medical diagnosis, electromagnetic wave absorption, toners in photocopying, conductive paints, drug delivery, rechargeable batteries etc (Suri *et al* 2001). Materials with nanoscale microstructure, i.e. nanocrystalline materials or nanocomposites, are increasingly becoming important for their technological importance due to their unique electrical, magnetic and optical properties. They can be distinguished from the nanocrystalline and nanophase materials on the basis that in case of nanocrystalline materials only one phase exists. While in the case of nanomaterials more than one Gibbson solid phases are present and out of which at least one of the phases is in the nanometer size range (Komaneni 1992). Earlier (Joshi *et al* 2002), energy band gap studies of these materials have been reported using absorption spectra. However, using thick pellets the effect of scattering in the absorption spectra cannot be properly estimated, as for computing the energy band gap, we could never experimentally obtain $(ahn)^2 = 0$ (Singh *et al* 2000). This problem can be solved by studying reflection spectra, where the exact value of energy band gap can be obtained as we may have $(ahn)^{2/3} = 0$. The reflection spectra of nanocomposite materials in the wavelength range 850–400 nm (Kumar *et al* 1999) have been used to determine the band gap.

2. Experimental

Nanocomposites of Ni–Zn ferrite in a copolymer matrix of aniline and formaldehyde were synthesized at room temperature by using a novel chemical method reported elsewhere (Mathur *et al* 1998). The nanocomposites of $Ni_{1-x}Zn_xFe_2O_4$ ferrites with x = 0·0, 0·2, 0·4, 0·6, 0·8 and 1·0 were synthesized in a copolymer matrix containing three different monomers of aniline and formaldehyde (*ortho*, *para* and *meta*). As a typical preparation, sample S1 (x = 0) was synthesized by treating the aqueous solution of aniline (0·10 mol), hydrochloric acid (0·12 mol), formaldehyde (0·10 mol) with an aqueous solution of halides of nickel (0·189 mol) taken according to the stoichiometry. The resulting solution was stirred thoroughly and added to 10% solution of NaOH. The precipitated composite was washed repeatedly with distilled water till the filtrate was free of alkali (pH 7·5) and then dried in air. Similarly, the samples S2–S6 (x = 0·2, 0·4, 0·6, 0·8 and 1·0) were synthesized using the same procedure by varying the quantities of nickel and zinc according to the stoichiometry. The reflection spectra of nanocomposites of Ni–Zn ferrite in a copolymer matrix of aniline and formaldehyde in presence of varying concentrations of zinc ions in bulk form were taken by spectrophotometer Hitachi model U-3400 at room temperature.

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3. Characterization of sample

The energy band gap of these materials is determined by the reflection spectra. According to the Tauc relation, the absorption coefficient, a, for direct band gap material is given by (Sirohi and Sharma 1999)

$$a\,hn = A\,(hn - E_g)^n, \quad (1)$$

where E_g the energy gap, constant A, is different for different transitions, (hn) is energy of photon and n is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the reflection. Also absorption coefficient, a, is directly proportional to $\ln\{(R_{max} - R_{min})/(R - R_{min})\}$ and is given by

$$2a\,t = \ln[(R_{max} - R_{min})/(R - R_{min})], \quad (2)$$

where t is the thickness of the sample, R_{max} and R_{min} are maximum and minimum values of reflectance, R the reflectance at a given photon energy, hn. To understand the nature of energy band gap transition in these materials, a graph of $\ln[hn \ln\{(R_{max} - R_{min})/(R - R_{min})\}]$ vs $\ln(hn - E_g)$ is drawn for the case of sample S6 as shown in figure 1. The plot in the figure is a straight line, the slope of which gives $n = 3/2$. This confirms that the transition is a forbidden direct transition in these materials.

When graph is plotted between $(a\,hn)^{2/3}$ or $[hn \ln\{(R_{max} - R_{min})/(R - R_{min})\}]^{2/3}$, and hn (as abscissa), a straight line is obtained. The extrapolation of the straight line to $(a\,hn)^{2/3} = 0$ axis gives the value of the band gap of the sample.

4. Results and discussion

Figure 2 shows the reflection spectra of nanocomposites of $Ni_{1-x}Zn_xFe_2O_4$ (with $x = 0{\cdot}6$). It is observed from figure 2 that reflection decreases with the decrease in wavelength. A sudden decrease at a particular wavelength, indicates the presence of optical band gap in these samples. These nanocomposites of Ni–Zn with copolymer matrix of aniline and formaldehyde in presence of varying concentrations of zinc ions are direct band gap materials and therefore the Tauc relation (Tauc 1974) as given in (1) is used for the determination of direct band gap in the nanocomposites of $Ni_{1-x}Zn_xFe_2O_4$. Graphs between $[hn \ln\{(R_{max} - R_{min}/R - R_{min})\}]^{2/3}$ vs hn have been plotted in figure 3. The extrapolation of

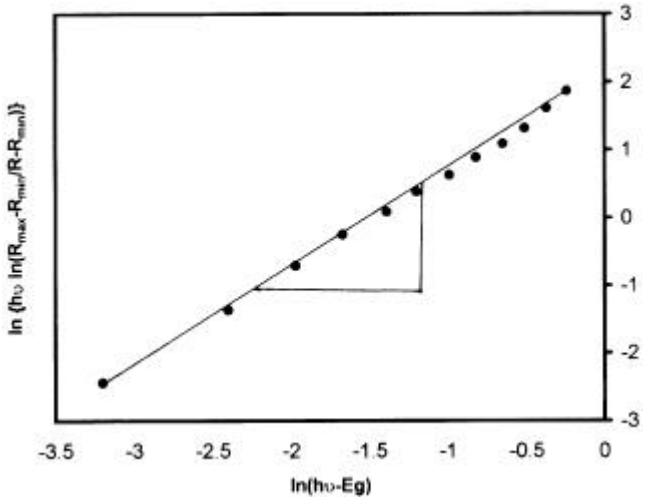

Figure 1. Plot of $\ln\{hn \ln(R_{max} - R_{min}/R - R_{min})\}$ vs $\ln(hn - E_g)$ (Tauc 1974).

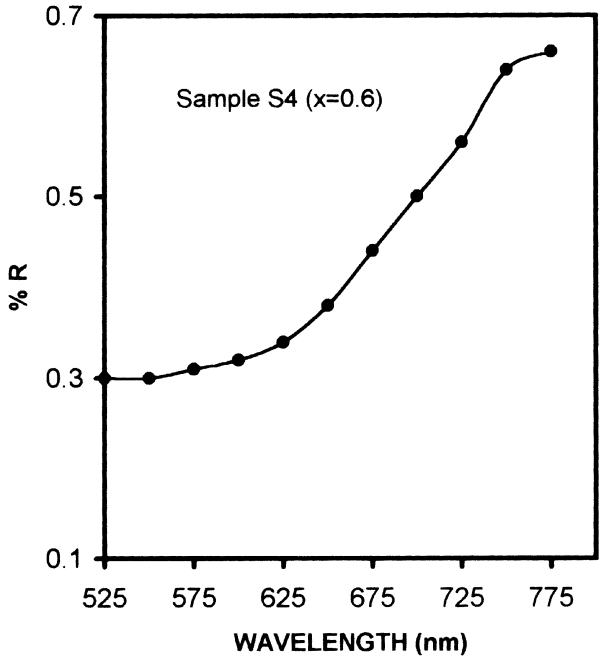

Figure 2. Reflection spectra of sample S4 (•) $Ni_{0.4}Zn_{0.6}Fe_2O_4$.

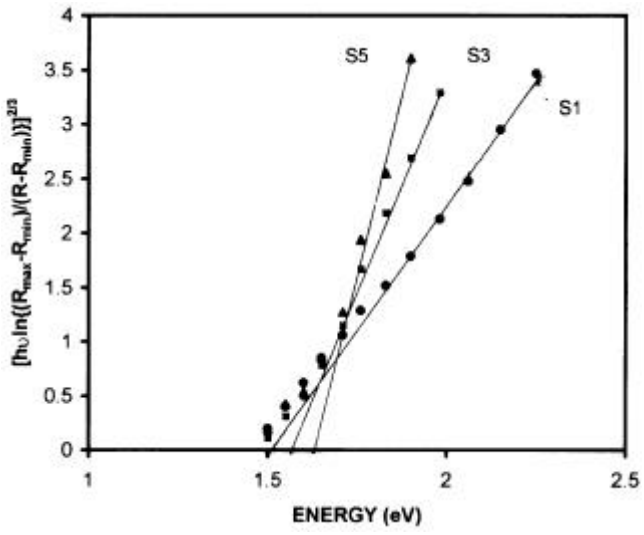

Figure 3. Band gap determination of sample S1 (•) $Ni_{1.0}Zn_{0.0}Fe_2O_4$; sample S3 (■) $Ni_{0.6}Zn_{0.4}Fe_2O_4$ and sample S5 (▲) $Ni_{0.2}Zn_{0.8}Fe_2O_4$.

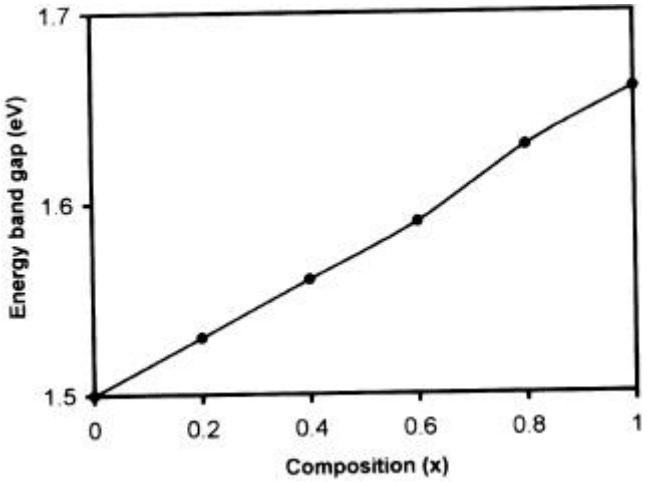

Figure 4. Band gap vs composition.

straight line to $[(a\,hn)]^{2/3} = 0$ gives the value of energy band gap. From these graphs, the value of energy band gap of sample S1 (composite of $Ni_{1-x}Zn_xFe_2O_4$ with $x = 0{\cdot}0$), S3 ($x = 0{\cdot}4$) and S5 ($x = 0{\cdot}8$) comes out to be 1·50, 1·56 and 1·63 eV, respectively. Similarly, for samples S2 (with $x = 0{\cdot}2$), S4 (with $x = 0{\cdot}6$) and S6 (with $x = 1{\cdot}0$), the obtained values of optical band gap are 1·53, 1·59 and 1·66 eV, respectively. The variation of optical band gap with x (different compositions) is given in figure 4. It can be observed from figure 4 that optical band gap increases continuously ($x = 0{\cdot}0$–$1{\cdot}0$) with the increase of Zn concentration in the nanocomposites of $Ni_{1-x}Zn_xFe_2O_4$. In some of the ternary semiconductors i.e. $InAs_xP_{1-x}$, it has been observed that energy band gap decreases with increase in the lattice parameter. Therefore, when we consider the variation of energy band gap with concentration of Zn in the above case, the increase in energy gap value with the increase of Zn concentration could be explained on the basis of decrease in lattice parameter due to increase in Zn concentration.

5. Conclusions

The experimentally observed band gap increase with the increase in the concentration of Zn suggests that the structural change occurring in the composite is responsible for such a variation.

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