

Bandgap determination of chemically doped polyaniline materials from reflectance measurements

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Received 3 February 2003; revised 1 April 2003; accepted 29 April 2003

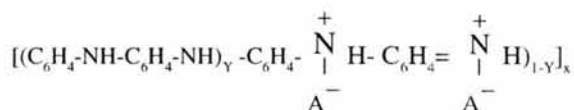
Spectroscopic techniques are very useful for characterizing semiconducting and conducting materials. The optical properties (specially reflection spectra) of polyaniline mix with metal Mn and Fe with different composition in bulk form were studied. The reflection spectra of these materials are recorded by a Hitachi spectro-photometer model (330), at room temperature, in the wavelength range 300-600 nm. From the analysis of reflection spectra, polyaniline mix with metal Mn and Fe have been found to have energy bandgap which decreases with increase of concentration of iron. An effort has also been made to study the structure formation using XRD techniques.

[Keywords: Bandgap, Polyaniline materials, Conducting polymers, Reflection spectra, Structure formation]

1 Introduction

Conducting polymers have found applications not only due to their electrical and thermal properties, but also due to their interesting optical properties. Conducting polymers in general and the polyaniline family of polymers in particular, have created intense scientific and technological interest. Conducting polymers have recently attracted a great deal of interest because of many applications in light-weight batteries, solar cells, electrochromic switching, variable transmission window, sensors and nonlinear optical materials^{1,2}. In polyaniline, basic chain structure exists in three insulating states: (i) locoemeraldine base (LB) (ii) emeraldine base (EB) and (iii) pernigraniline base (PN) forms of polyaniline. The energy gaps in LB and EB originate from the electronic structure of the backbone C₆H₄ units. The gaps in LB and EB rules out a bond alternation defect description of the charge-states of polyaniline materials. Significant consequences of the ring-rotational degrees of freedom exist for the electronic structure and defect states of polyaniline^{3,4}. Chemical formula of PANI is $[(-B-NH-B-NH-)_y(-B-N=Q=N-)_x]_z$, in which B and Q denote the C₆H₄ rings in the benzenoid and quinoid forms, respectively. When emeraldine base is equilibrated in a large excess of aqueous-acid solution,

protonation occurs at imine repeat unit to produce emeraldine salt of polyaniline (PA-ES) believed to have the composition where A⁻ is the anion and consists of equal number of reduced $[C_6H_4-NH-C_6H_4-NH]$ and $[C_6H_4-N=C_6H_4=N-]$ repeat units⁵. The positively charged nitrogen portion is related to the doping level. In other words, protonation level of the blends plays an important role in thermal as well as optical conduction of these materials⁶.



2 Experimental Details

Polyaniline is usually prepared by redox polymerization of aniline using ammonium perdisulphate, (NH₄)₂S₂O₈, as an oxidant. Distilled aniline (0.02 M) is dissolved in 300 ml of pre-cooled HCl (1.0 M) solution, maintained at 0.5 °C. A calculated amount of ammonium perdisulphate (0.05 M) dissolved in 200 ml of HCl (1M), pre-cooled to 0-5 °C, is added to the above solution. The dark green precipitate (ppt) resulting from this reaction is washed with HCl (1.0 M) until the green colour disappears. This ppt is further extracted with

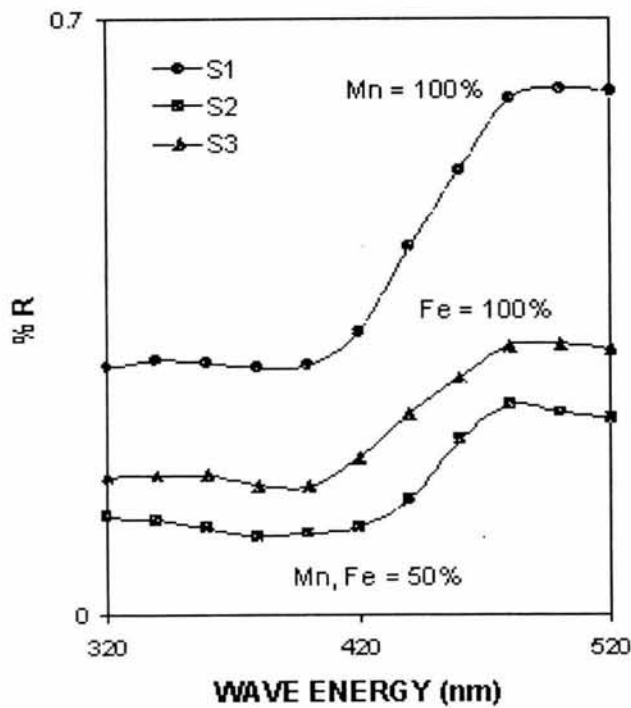


Fig. 1 — Reflection spectra of Sample S1 to S3

Table 1 — 2θ , d value and lattice parameters for the samples

	2θ	d (Å)	(h,k,l)
Sample S1 (Mn = 100%)	31.67	2.82	(2 0 0)
	36.04	2.48	(0 0 2)
	45.41	1.94	(2 2 0)
	56.39	1.63	(3 1 1)
Sample S2 (Mn, Fe = 50%)	59.76	1.54	(1 1 3)
	31.62	2.82	(2 0 0)
	45.36	1.99	(2 2 0)
Sample S3 (Fe = 100%)	31.66	2.82	(2 0 0)
	45.39	2.00	(2 2 0)
	56.44	1.63	(3 1 1)

tetra-hydrofuran and NMP (N-Methyl Pyrrolidinone) solution by soxhlet extraction and dried to yield the emeraldine salt. Emeraldine base can be obtained by heating the emeraldine salt with ammonia solution. Simultaneously, separate salt solution is prepared by dissolving the MX (M=Metal and X=Halide) in distilled water. The solution is then slowly added to the precooled polymer solution with constant stirring.

This composite is then dried in an oven, at high temperature, to get the conducting polymer in the powder form. The powder, so obtained, can be used for device fabrication. As a typical preparation, sample S1 (Mn=100

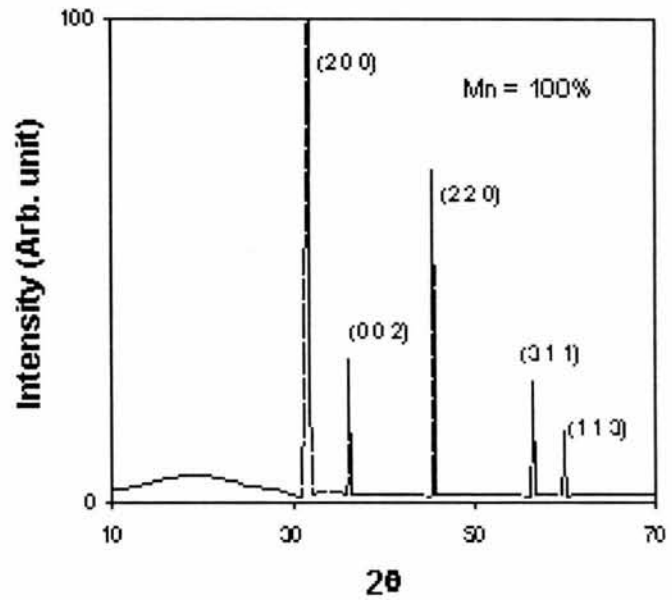


Fig. 2 — XRD of the sample S1 (Mn = 100%)

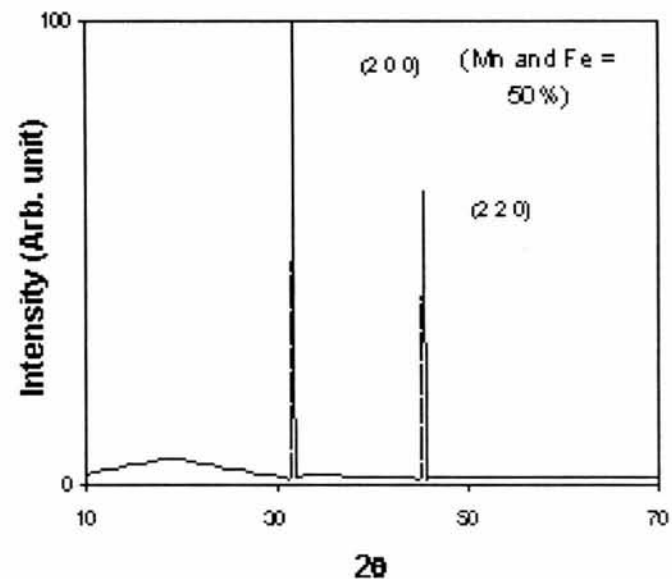


Fig. 3 — XRD of the sample S2 (Mn, Fe = 50%)

%) was synthesized by treating the aqueous solution of aniline, hydrochloric acid, and Mn taken according to the stoichiometry. The resulting solution was stirred thoroughly and added to solution of alkali. 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-S3 (Mn=50, 0 % and Fe = 50, 100 %) were synthesized using the same procedure by varying the quantities of Mn and Fe according to the stoichiometry. Pellets of thickness 1 mm and diameter 12 mm were prepared from the powdered materials by a pressure of 4.33×10^8 Pascal.

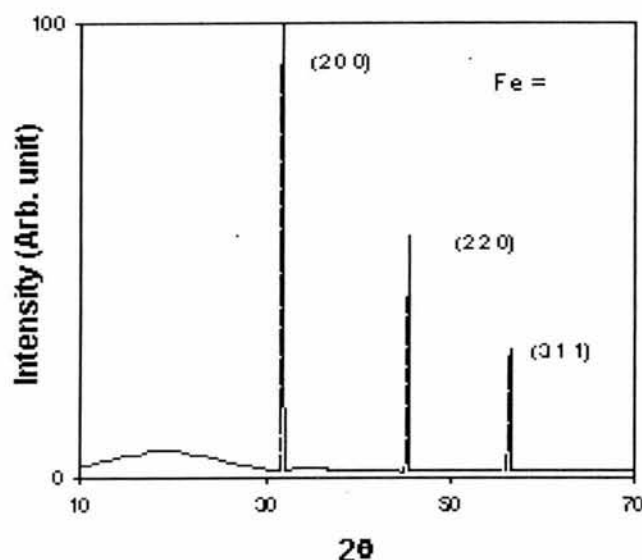


Fig. 4 — XRD of the sample S3 (Fe = 100%)

3 Characterization of Sample

The reflection spectra of polyaniline mix with metal Mn and Fe in bulk form were taken by spectrophotometer Hitachi model (330), at room temperature. In this model, the prism/grating double monochromatic system is used. The energy bandgap of these materials is determined by reflection spectra. Almost all the samples have direct bandgap. According to the Tauc relation, the absorption coefficient α for direct bandgap material is given by⁷:

$$\alpha h\nu = A (h\nu - E_g)^n \quad \dots(1)$$

$$2\alpha t = \ln \left(\frac{R_{\max} - R_{\min}}{R - R_{\min}} \right) \quad \dots(2)$$

where, R is the reflection for any intermediate energy photon ($h\nu$). Constant A , is different for different transitions, E_g the energy gap and t is the thickness of the sample.

A graph is plotted between $(\alpha h\nu)^2$ or the square of $h\nu \ln [R_{\max} - R_{\min} / (R - R_{\min})]$, and $\alpha h\nu$ (as abscissa), a straight line is obtained. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$ axis gives the value of the bandgap of the sample.

4 Results and Discussion

Reflection spectra of polyaniline mix with metal Mn and Fe with different composition is shown in Fig. 1. It is observed from Fig. 1 that, reflection decreases with the decrease in wavelength. Sudden fall present at a particular wavelength, indicates the presence of optical

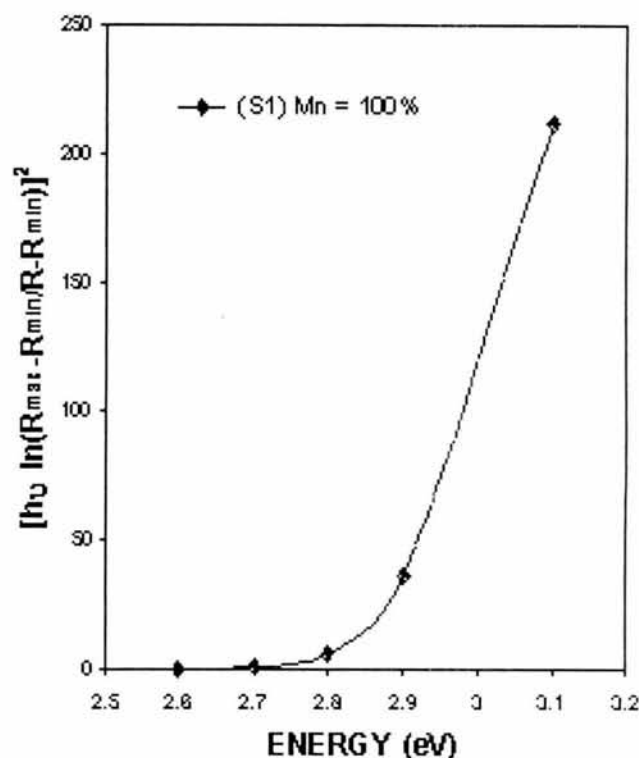


Fig. 5 — Bandgap determination of Sample S1 Mn (100%)

bandgap in these samples.

XRD of samples as shown in Figs 2-4 have been used to characterize the samples. The X-ray diffraction pattern gives valuable information about the nature and structure of the samples.

Sample containing Fe as dopant is polycrystalline. Peak position suggests that lattice structure may be cubic. Calculated value of lattice parameter $a = 5.64 \text{ \AA}$. In sample containing only Mn, XRD pattern suggests that, the lattice may be tetragonal. Calculated values of lattice parameters $a = b = 5.64 \text{ \AA}$ and $c = 4.98 \text{ \AA}$. When we have Mn and Fe as doped metals, then again, it is cubic lattice. Table 1 gives the 2θ , d value and lattice parameters for the samples.

Tauc relation as given in Eq. (2) is used for the determination of energy bandgap in the polyaniline mix with metal Mn and Fe. Fig. 5 shows the representative curve between $[h\nu \ln (R_{\max} - R_{\min} / (R - R_{\min}))]^2$ and $h\nu$ for the determination of bandgap of sample S1. The extrapolation of straight line to $[(\alpha h\nu)]^2 = 0$ gives the value of energy bandgap. From Fig. 5, the value of energy bandgap of sample S1 (Mn=100%) comes out to be 2.86 eV. In the same manner, the value of energy bandgap of samples S2 (Mn, Fe=50%) and S3 (Fe=100%) comes out to be 2.79 and 2.77 eV, respectively. It is observed that,

energy bandgaps decrease suddenly, when metal Fe is doped in the matrix. This might be due to the fact that, Fe additive in increasing concentration produces some kind of structural change in the sample. XRD data suggests that, with only Mn as dopant, the structure has tetragonal lattice, whereas when Mn is replaced by Fe, the structure changes to cubic lattice. Therefore, energy bandgap suddenly increases when only Mn is present.

5 Conclusions

Decrease in the bandgap with increase of concentration of Fe in polyaniline doped with Mn is suggestive of the fact that, lattice structure changes from tetragonal to cubic.

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