Optical Band Gap Determination of Ni-Al Doped Polyaniline at Room Temperature and Different Annealing Temperatures

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Abstract. Spectroscopic techniques are very useful for characterizing semiconducting and conducting materials. The optical properties (specially reflection spectra) of polyaniline mix with metal Ni and Al 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 Ni and Al have been found to have energy bandgap which decreases with increase of concentration of Al. an effort has also been made to study the structure formation using XRD techniques.

IndexTerms: Bandgap, Conducting polymers, Reflection spectra.

1. Introduction
Polyaniline (PANI) in its emeraldine oxidation state has attracted considerable interest due to its environmental stability, electrical conductivity and thermal conductivity and has emerged as promising materials for application in various states [1-5]. Unlike other conducting polymer, PANI can also be reversibly modified by pH change (with the conducting emeraldine salt being doped by base to the insulating emeraldine base form) as well as oxidized and reduced to pernigraniline and leucoemeraldine forms. Chemical formula of PANI is \[\left[\left(-B-NH-B-NH-\right)^Y\left(-B-N=Q=N-\right)^1-Y\right]^X\] in which B and Q denote the C\(_6\)H\(_4\) 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 \[
\left[\left(C_{6}H_{4}^+-NH-C_{6}H_{4}-NH\right)^{\frac{\pm}{A}}\left(C_{6}H_{4}^+-NH-C_{6}H_{4}=NH\right)^{\frac{\pm}{A}}\right]^X
\]
where \(A^-\) is the anion and consists of equal number of reduced \([C_{6}H_{4}-NH-C_{6}H_{4}-NH]\) and \([C_{6}H_{4}-N=C_{6}H_{4}=N]\) repeat units.

This results in the increased thermal as well as electrical conductivity. However, conductivity is affected by the protonation, level of oxidation, moisture contact, and polymerization conduction [6-10]. Due to their chemical stability, their high conductivity upon doping and their non-linear optical properties, polypyrrole (PPy) and polythiophene (PTh) are among the most widely studied conducting polymers, experimentally and theoretically. Since PPy and PTh have relatively large band gaps, 2.85
and 2.0 eV, respectively, the neutral forms are insulator [11-14]. Further, the present paper deals with the characterization of material through XRD, optical measurements carried out systematically on polyaniline doped with metal Ni and Al with different concentration as function of different temperature (room temperature – 170°C). The detailed analysis of the observed experimental data indicates the operation of the interesting relaxation phenomenon in the doped conducting polymers.

2. Experimental procedure

Polyaniline is usually prepared by redox polymerization of aniline using ammonium perdisulphate, (NH₄)₂S₂O₈, as an oxidant. Distilled aniline (0.02M) is dissolved in 300ml of precooled HCl (1.0M) solution, maintained at 0.5°C. A calculated amount of ammonium perdisulphate (0.05 M) dissolved in 200ml of HCl (1.0 M), precooled 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 color disappears. This ppt is further extracted with tetra hydrofuran and NMP (N- Methyl Pyrolidinone) solution by soxhlet extraction and dried to yield the emeraldine salt. Emeraldine base can be obtained by heating the emeraldine salt with ammonia solution. This composite is then dried in an oven at high temperature to get the conducting polymer in powder form. The powder so obtained can be used for device fabrication. As a typical preparation, sample S1 (Ni = 100 %) was synthesized by treating the aqueous solution of aniline, hydrochloric acid and Ni 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-S4 (Ni = 100, 90, 80 % and Al = 0, 10, 20 %) were synthesized using the same procedure by varying the quantities of Ni and Al according to the stoichiometry. Pellets of thickness 2 mm and diameter 12 mm were prepared from the powdered materials by a pressure of \(4.33 \times 10^8\) Pascal. The Sample holder (Fig. 1) containing these samples is placed in a furnace having sensitivity of 1K. After achieving the isothermal conditions in the sample, a constant current pulse is passed through the heating element.

![Figure 1. Sample holder](image)

2.1. Characterisation of sample

The reflection spectra of polyaniline mix with metal Ni and Al 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 band gap of these materials is determined by the reflection spectra. According to the Tauc relation, the absorption coefficient \(\alpha\), for direct band gap material is given by [15,16].
\[ \alpha h\nu = A (h\nu - E_g)^n \] \hspace{1cm} \ldots(1) 

Where \( E_g \) is the energy gap, constant \( A \), is different for different transitions, \( (h\nu) \) 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 \( \alpha \) is directly proportional to \( \ln \left( \frac{(R_{\text{max}} - R_{\text{min}})}{(R - R_{\text{min}})} \right) \) and is given by

\[ 2\alpha t = \ln \left( \frac{(R_{\text{max}} - R_{\text{min}})}{(R - R_{\text{min}})} \right) \] \hspace{1cm} \ldots(2) 

Where \( t \) is the thickness of the sample, \( R_{\text{max}} \) and \( R_{\text{min}} \) are maximum and minimum values of reflectance, \( R \) the reflectance at a given photon energy, \( h\nu \). When graph is plotted between \( (\alpha h\nu)^2 \) or \([h\nu \ln \left( \frac{(R_{\text{max}} - R_{\text{min}})}{(R - R_{\text{min}})} \right)]^2\), vs \( h\nu \) (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 band gap of the sample.

### 3. Results and discussion

Reflection spectra of polyaniline mix with metal Ni and Al with different composition (sample S2 and S3) is shown in Figure 2.

![Reflection spectra of Sample S2 and S3](image)

Figure 2. Reflection spectra of Sample S2 and S3

It is observed from fig. 2 that reflection decreases with the decrease in wavelength. Sudden fall present at a particular wavelength indicates the presence of optical band gap in this samples. XRD of samples as shown in Fig 3-4 have been used to characterize the samples. The X-ray diffraction pattern gives valuable information about the nature and structure of the sample. Sample containing Ni as dopant is polycrystalline. Peaks position suggests that lattice structure may be tetragonal. Calculated value of lattice parameter \( a = b = 5.92 \) \( \text{Å} \) and \( c = 5.04 \) \( \text{Å} \). in sample containing only Al, XRD pattern suggests that the lattice may be tetragonal. Calculated values of lattice parameters \( a = b = 6.52 \) \( \text{Å} \) and \( c = 5.64 \) \( \text{Å} \). Table 1 gives the 20, d value and plane indices for the sample Ni (100%) and Al (100%). XRD data suggest that with only Ni as dopant the structure have tetragonal lattice, whereas when Ni is replaced by Al, the structure remains for same. Table 1 gives the 20, d value and lattice parameters for the samples.
Figure 3. XRD of the sample S1 (Ni = 100%)

Figure 4. XRD of the sample (Al = 100%)

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

| Sample               | 2θ  | d(A₀) | (h,k,l) |
|----------------------|-----|-------|---------|
| Sample S1 (Ni = 100%)| 30.16 | 2.96  | (2 0 0) |
|                      | 35.62 | 2.52  | (0 0 2) |
|                      | 42.97 | 2.10  | (2 2 0) |
|                      | 57.26 | 1.61  | (1 1 3) |
|                      | 62.56 | 1.48  | (4 0 0) |
| Sample (Al = 100%)   | 27.37 | 3.26  | (2 0 0) |
|                      | 31.76 | 2.82  | (0 0 2) |
|                      | 45.50 | 1.99  | (3 1 1) |
|                      | 56.52 | 1.63  | (4 0 0) |
|                      | 66.27 | 1.41  | (3 1 3) |

Tauc relation as given in Eq. (2) is used for the determination of energy band gap in the polyaniline mix with metal Ni and Al.
**Figure 5.** Band gap determination of sample S1 (Ni = 100%)

**Figure 6.** Band gap determination of sample S2 (Ni = 90% and Al = 10%).

**Figure 7.** Band gap determination of sample S3 (Ni = 80% and Al = 20%).
Figure 5 to Figure 8 shows the representative curve between \( [h\nu \ln (R_{\text{max}} - R_{\text{min}}) / (R - R_{\text{min}})]^2 \) vs \( h\nu \) for the determination of band gap of sample S1 to S4. The extrapolation of straight line to \((\alpha h\nu)^2 = 0\) gives the value of energy band gap. From figure 5, 6, 7 and 8, the value of energy band gap of sample S1 (Ni = 100%), S2 (Ni = 90% and Al = 10%), S3 (Ni = 80% and Al = 20%) and S4 (Ni = 70% and Al = 30%) comes out to be 2.90 eV, 2.84 eV, 2.75 eV and 2.68 eV, respectively.

It is observed that energy band gaps decrease suddenly when metal Al is doped in the matrix. Sample S1 (Ni = 100%), S2 (Ni = 90% and Al = 10%), S3 (Ni = 80% and Al = 20%) and S4 (Ni = 70% and Al = 30%) were annealed at 50, 80, 100, 110, 120, 130, 140, 150 and 170 °C for two hours. Energy band gap of these samples using above technique were measured. Table 2 is shown experimental and theoretical value of energy band gap of samples at different annealing temperature. Figure 9 shows variation of energy band gap with annealing temperature.
Table 2. Experimental and theoretical value of energy band gap of samples at different annealing temperature.

| Annealing Temperature (°C) | Sample S1 (Ni = 100%) | Sample S2 (Ni = 90% and Al = 10%) | Sample S3 (Ni = 80% and Al = 20%) | Sample S4 (Ni = 70% and Al = 30%) |
|---------------------------|-----------------------|----------------------------------|-----------------------------------|----------------------------------|
|                          | Exp. | Theo. | Exp. | Theo. | Exp. | Theo. | Exp. | Theo. |
| 50                       | 2.82 | 2.82  | 2.77 | 2.77  | 2.68 | 2.68  | 2.62 | 2.62  |
| 80                       | 2.74 | 2.71  | 2.64 | 2.59  | 2.61 | 2.57  | 2.57 | 2.55  |
| 100                      | 2.65 | 2.61  | 2.57 | 2.53  | 2.54 | 2.50  | 2.52 | 2.49  |
| 120                      | 2.57 | 2.55  | 2.52 | 2.50  | 2.48 | 2.45  | 2.46 | 2.44  |
| 130                      | 2.54 | 2.54  | 2.49 | 2.49  | 2.44 | 2.44  | 2.42 | 2.41  |
| 140                      | 2.58 | 2.56  | 2.53 | 2.50  | 2.46 | 2.45  | 2.40 | 2.40  |
| 150                      | 2.67 | 2.59  | 2.60 | 2.54  | 2.53 | 2.49  | 2.43 | 2.41  |
| 170                      | 2.76 | 2.76  | 2.73 | 2.73  | 2.62 | 2.62  | 2.51 | 2.51  |

The minimum value is observed at around 130°C for sample S1 to S3 and 140°C for sample S4. Thermophysical studies on these samples suggest that at 130°C and 140°C effective thermal conductivity and effective thermal diffusivity are maximum [17]. Thus, the material annealed at 130°C and 140°C shows the lowest band gap, which is also confirmed through thermal conductivity measurements.

An empirical relation for the variation of energy band gap with the annealing temperature has also been developed. The relation is given by

\[ E_g (\tau) = E_g (\tau_0) + D (\tau - \tau_0)^2 + E (\tau - \tau_0)^3 \]  \( \ldots(3) \)

Where D and E are constants calculated by experimental conditions and their values are \( D = 1.1 \times 10^{-4} \text{ eV/K}^2 \) and \( E = 7.8 \times 10^{-7} \text{ eV/K}^3 \) for sample S1, \( D = 5.0 \times 10^{-5} \text{ eV/K}^2 \) and \( E = 8.9 \times 10^{-7} \text{ eV/K}^3 \) for sample S2, \( D = 8.8 \times 10^{-5} \text{ eV/K}^2 \) and \( E = 6.3 \times 10^{-7} \text{ eV/K}^3 \) for sample S3 and \( D = 9.8 \times 10^{-6} \text{ eV/K}^2 \) and \( E = 7.9 \times 10^{-7} \text{ eV/K}^3 \) for sample S4, \( \tau \) is the different annealing temperature of the samples. \( E_g (\tau_0) \) is the minimum value of energy band gap. Where \( \tau_0 = 130^\circ \text{C} \) and \( 140^\circ \text{C} \) for sample S1 to S3 and S4 respectively.

4. Conclusions

As the structural changes in the samples take place on annealing, similar to the thermal conduction increase in electrical conductivity is expected up to 130°C and 140°C, this may be attributed to the increase in carrier concentration hence decrease in energy band gap. Decrease in the band gap with the increase of concentration of Al in polyaniline doped with Ni is suggestive of the fact the lattice structure remain for same. The minimum value is observed at around 130°C for sample S1 to S3 and 140°C for sample S4. Thermophysical studies on these samples suggest that at 130°C and 140°C effective thermal conductivity and effective thermal diffusivity are maximum. It is observed that energy band gaps decrease suddenly when metal Al is doped in the matrix. Sample S1 (Ni = 100%), S2 (Ni = 90% and Al = 10%), S3 (Ni = 80% and Al = 20%) and S4 (Ni = 70% and Al = 30%) were annealed at 50, 80, 100, 110, 120, 130, 140, 150 and 170°C for two hours. The optical properties (specular reflection spectra) of polyaniline mix with metal Ni and Al with different composition in bulk form were studied. The reflection spectra of these materials are recorded by a Hitachi spectrophotometer model (330), at room temperature, in the wavelength range 300-600 nm. From the analysis
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