**Analysis of Optical Band Gap**, **DC Conductivity and Activation Energy in Barium-Doped Lanthanum Manganite Nanoparticles Tailored with Polypyrrole**

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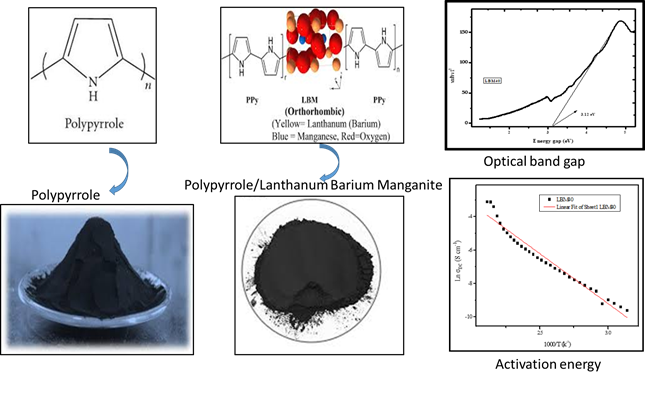
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**Abstract:** The study investigates the effect of incorporating La₀.₇Ba₀.₃MnO₃ (LBM) perovskite nanoparticles into a polypyrrole (PPy) matrix at varying weight percentages (10%, 20%, 30%, 40%, and 50%) on both the DC electrical conductivity and optical band gap of the resulting nanocomposites. Optical absorption measurements were carried out using UV-Visible spectroscopy in the range of 200–600 nm. The UV-Vis spectra revealed a prominent absorption peak at approximately 315 nm for composites containing 10% and 20% LBM. However, with increasing LBM content (30%, 40%, and 50%), the absorption peak progressively red-shifted to longer wavelengths, appearing at 320 nm, 325 nm, and 335 nm, respectively. The optical band gap increased for PPy/LBM10, and PPy/LBM20, while it gradually decreased for the higher LBM compositions (PPy/LBM30, PPy/LBM40, and PPy/LBM50). The variation in band gap can be attributed to the quantum confinement effect. The DC conductivity show semiconductor behavior of the composites. The activation energy is found to be high for PPy/LBM20 composite. These findings suggest that the inclusion of LBM modifies the optical properties and band gap of PPy, which could have potential applications in organic devices operating at high frequencies and voltages.

**Keywords:** Perovskite, Polypyrrole, Chemical oxidation, Optical band gap*,* DC conductivity

**Graphical abstract**



1. **Introduction**

Nanocomposite research is advancing rapidly due to the exceptional multifunctional properties of these materials and their broad applicability across fields such as electronics, energy, environmental science, and biomedicine. Among these, wide bandgap semiconductors, have attracted considerable interest, as they support efficient operation under extreme conditions such as high temperatures, high frequencies, and high voltages making them ideal candidates for next-generation electronic and power devices. Investigations into the optical band gap of such materials are particularly relevant for applications in light-emitting diodes (LEDs), optoelectronics, and energy storage systems. Typically, wide bandgap materials exhibit energy gaps in the range of 2–4 eV, compared to traditional semiconductors, which range between 0.7–1.1 eV. Semiconductors with tailored bandgaps, achieved through doping and composite formation, are considered ideal for various functional applications **[1–2].**

In this study, we focus on polypyrrole (PPy), an intrinsically conducting polymer noted for its excellent environmental stability, good electrical conductivity, mechanical strength, and versatile optical and magnetic characteristics. The polymerization and resulting properties of PPy are highly sensitive to synthesis parameters such as solvent type, monomer concentration, doping level, electrochemical conditions, and temperature **[3–5].** On the other hand, perovskite-based ceramic materials with the general formula ABO₃—such as BaTiO₃, LaMnO₃, and SrTiO₃—have emerged as promising candidates for applications in electronics, spintronic, magnetic sensing, and energy storage. These materials offer unique ferroelectric, piezoelectric, and magneto resistive behaviors, which make them attractive for multifunctional device applications.

Combining PPy with ABO₃-type ceramics in nanocomposite systems presents an effective strategy to integrate the processability and conductivity of polymers with the advanced functional properties of perovskites. Such hybrid systems are being explored for applications including flexible capacitors, electromagnetic interference (EMI) shielding, multifunctional sensors, and high-performance energy storage devices. In this work, we have selected barium doped lanthanum manganite (La₀.₇Ba₀.₃MnO₃, or LBM) due to its well-defined orthorhombic crystal structure and reported optical band gap of ~3.89 eV **[6–7].**

The objective of our study is to investigate the optical band gap and activation energy of PPy/LBM nanocomposites. These are key parameters that determine a material’s suitability for optoelectronic applications. The optical band gap, defined as the energy difference between the valence and conduction bands, governs a material’s interaction with light. For the study of PPy/LBM system, the band gap is assessed via UV-Visible spectroscopy using Tauc plot analysis. Incorporation of LBM into the PPy matrix can lead to band gap modulation often resulting in a reduced optical band gap due to enhanced π–π\* conjugation, increased carrier delocalization, and the creation of localized states at the interface. Activation energy, on the other hand, reflects the minimum energy required for charge carrier transport. It is typically determined from temperature dependent conductivity measurements using the Arrhenius relation. The inclusion of LBM nanoparticles, known for their colossal magnetoresistance and mixed-valence manganese states (Mn³⁺/Mn⁴⁺), enhances electronic transport by providing additional hopping sites and reducing the energy barriers for conduction. A lower activation energy signifies more efficient charge movement, which is advantageous for devices that operate under variable thermal or voltage conditions. The synergic interaction between PPy and LBM in the nanocomposite structure results in favorable modifications to both optical and electrical properties. This includes a tunable band gap and reduced activation energy, both of which are critical for advancing high-performance optoelectronic devices. Our findings highlight the potential of PPy/LBM composites in the development of organic-based transistors, photodetectors, and solar cells capable of operating efficiently at elevated voltages **[8–9].**

**2. Material and methods**

**2.1. Synthesis of La₀.₇Ba₀.₃MnO₃ (LBM) Nanoparticles**

La₀.₇Ba₀.₃MnO₃ (LBM) nanoparticles were synthesized via the sol–gel method. Analytical-grade lanthanum oxide (La₂O₃), Barium carbonate (BaCO₃), and Manganese Carbonate (MnCO₃) (Sigma-Aldrich, 99%) were used as starting materials in stoichiometric ratios. These precursors were dissolved in nitric acid and subsequently diluted with deionized water in a 1:3 volume ratio (10 mL nitric acid to 30 mL water) under continuous magnetic stirring to ensure homogeneity. To initiate the gel formation, 30 mL of polyethylene glycol (PEG) was added to the solution as a polymerizing agent. The resulting mixture was heated on a hot plate: initially at 60 °C for 1 hour to promote polymerization, followed by a gradual increase to 100 °C to remove volatile components. The temperature was then raised to 250 °C and maintained for 2 hours to facilitate the formation of a dry, organic-rich gel. The dried gel was finally calcined in a muffle furnace at 700 °C for 5 hours to produce phase-pure, crystalline LBM nanoparticles.

**2.2. Synthesis of Polypyrrole (PPy)**

Polypyrrole (PPy) was synthesized via an in situ chemical oxidative polymerization method. Pyrrole monomer (0.3 M) was dissolved in 100 mL of distilled water in a round-bottom flask equipped with a magnetic stir bar. The flask was placed in an ice bath to maintain the reaction temperature between 0–5 °C and set on a magnetic stirrer operating at 400 rpm. A separate solution of ammonium persulfate (APS, 0.6 M), serving as the oxidizing agent, was prepared by dissolving APS in 100 mL of distilled water. This solution was transferred to a burette and added dropwise to the pyrrole solution over the course of the reaction, which was continued for 5 hours under the same low-temperature conditions. Upon completion of the reaction, a black precipitate of PPy was formed. The product was washed thoroughly with acetone to remove unreacted residues and filtered using a vacuum pump. The resulting solid was dried in a hot air oven pre-set to 100 °C. Once the oven reached the desired temperature, it was switched off, and the sample was left inside overnight to ensure gradual drying. To remove residual moisture, the partially dried PPy was subsequently heated in a muffle furnace at 100 °C for an additional 2 hours. The final product was ground into a fine powder and stored for further analysis. The yield of polypyrrole obtained was 2.9 g, which was taken as 100% weight percentage for subsequent composite synthesis.

### **2.3. Synthesis of Polypyrrole/La₀.₇Ba₀.₃MnO₃ (PPy/LBM) Nanocomposites**

Polypyrrole/La₀.₇Ba₀.₃MnO₃ (PPy/LBM) nanocomposites were synthesized using an in situ chemical oxidative polymerization technique. Pyrrole monomer (0.3 M) was dissolved in 100 mL of distilled water in a round-bottom flask containing a magnetic stir bar. The flask was placed in an ice bath filled with ice pellets to maintain the temperature between 0 and 5 °C. This setup was positioned on a magnetic stirrer, and the stirring speed was set to 400 rpm. A 0.6 M aqueous solution of ammonium persulfate (APS), serving as the oxidant, was prepared in 100 mL of distilled water and loaded into a burette. This solution was added dropwise to the pyrrole mixture. Simultaneously, 10 wt% of LBM Nano powder (calculated with respect to the weight of pyrrole, considered as 100 wt%) was added to the reaction mixture. The polymerization reaction was allowed to proceed for 5 hours while maintaining the temperature at 0–5 °C. The resulting black precipitate was washed thoroughly with acetone to remove unreacted monomers and byproducts. It was then filtered using a vacuum pump and dried in a hot air oven at 100 °C for 3 hours. To ensure complete removal of residual moisture and enhance the crystallinity, the dried powder was further heat-treated in a muffle furnace at 100 °C for 2 hours. The final product was ground into a fine powder and stored for further characterization. The yield of the PPy/LBM10 nanocomposite was recorded as 2.54 g.

Following the same procedure, additional nanocomposites; PPy/LBM20, PPy/LBM30, PPy/LBM40, and PPy/LBM50—were synthesized by varying the LBM Nano powder content to 20%, 30%, 40%, and 50% (by weight relative to pyrrole), respectively.

The characterization studies of the compounds like Scanning Electron Microscopy [SEM], Transmission Electron Microscopy [TEM] and X-ray Diffraction [XRD], Fourier transform Infrared spectroscopy [FTIR] studies are discussed in detail in our previous published journal article and chapter **[10-11].**

**3. Results and Discussion**

**3.1. Optical absorption of PPy/LBM nano compound**

To investigate the optical properties of the prepared composites, UV-Visible absorption measurements were carried out using a Cary 5000 instrument, recording data within the range of 200 nm to 1000 nm in the absorption mode. This study has valuable insights into the interatomic transitions within the nanocomposite containing polypyrrole at room temperature. Figure 1. below show the absorption wavelengths for pure LBM and PPy/LBM compounds. The absorbance peak observed at 210 nm is ascribed as the O-H molecule absorption **[12]**, while the peaks at 370 nm and 390 nm correspond to π-π\* transitions happening inside the benzoid ring **[13-14]** corresponds to weak polaron transitions and the latter to bipolaron transitions, which arise from the increased filler content of LBM.



**Figure 1. Spectral absorbance PPy/LBM composites**

This suggests a strong interaction allying PPy and the LBM nanoparticles, enhancing the polymer chain formation through effective monomer linking.

UV-Vis spectroscopy of PPy/LBM composites containing 10% and 50% LBM by weight reveals noticeable shifts in peak positions, indicating that LBM nanoparticles substantially influence the optical absorption characteristics of the PPy chains. All composites exhibit a broad absorption tail extending from approximately 400 nm to 1000 nm, which is likely attributable to structural defects or synthesis-related impurities **[15].** Additionally, the presence of distinct absorption peaks in the 250–390 nm region confirms strong optical absorption in the UV range **[16],** suggesting potential for applications such as nonlinear frequency conversion and ultraviolet (UV) photodetectors.

These findings demonstrate that the incorporation of LBM not only alters the optical transitions within the PPy matrix but also broadens the absorption window, enhancing the composite’s suitability for optoelectronic applications.

**3.2. Energy Gap Calculation**

The essence of a semiconductor's band gap, whether direct or indirect, can be deduced from the shapes of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the constituent conjugated monomers. Since polypyrrole has conjugated double bonds and a non-degenerate ground state, its transitions are classified as indirect band gap transitions. Consequently, determining the optical band gap of any composite is essential, as the energy gap offers valuable insights into the material's optical properties. These features are reproving for understanding the optical conductivity of the samples **[17-18].** The optical band gap is commonly analyzed using Tauc's plot **[15]**, which correlates the photon energy absorption coefficient through the following equation

(α h υ) 2 α (h υ -Eg) ………… (1)

Where α and Eg are absorption coefficient and energy gap (eV), h and υ represents Planck’s constant and frequency of radiation respectively.

The power in the equation is considered as 2, by considering the semiconductor as indirect semiconductor. Using the reflectance data recorded in the said wavelength energy gap Eg is determined by using the Kubelka – Munk (K–M) method having the expression

 …………..(2)

Where α and R are the absorption coefficient and reflectance respectively

To find the energy band gap, the plot of photon absorption co efficient with energy gap is plotted using the reflectance data **[19-20]**. The graphs obtained for PPy/LBM composites are shown in the figures 2 (a-e).

**Figure 2.a. Optical band gap of PPy/LBM10 2.b. Optical band gap of PPy/LBM20**

**2.c. Optical band gap of PPy/LBM30 2.d. Optical band gap of PPy/LBM40**



**2.e. Optical band gap of PPy/LBM50**

One key observation from the Figure 2.a–e is the slight variation in the optical band gap with increasing LBM content in the PPy matrix. As summarized in Table 1, the band gap decreases marginally as the weight percentage of LBM increases, suggesting a modulation of the electronic structure of the composites. This variation in band gap can be attributed to the quantum confinement effect, a quantum mechanical phenomenon that becomes significant at the nanoscale. The electronic transition responsible for the band gap occurs between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the conjugated PPy polymer and is influenced by the presence of LBM nanoparticles. The observed changes indicate a clear interaction between the PPy chains and the LBM dopant, likely due to charge transfer or electronic coupling effects that alter the energy levels of the composite system.

**Table 1: Optical Band gap of PPy/LBM**

**nano composites**

|  |  |
| --- | --- |
| **Name of the compound** | **Optical band gap (eV)** |
| PPy/LBM10 | 3.09 |
| PPy/LBM20 | 3.01 |
| PPy/LBM30 | 3.14 |
| PPy/LBM40 | 3.12 |
| PPy/LBM50 | 3.08 |

**3.4. DC conductivity studies of PPy, and PPy/LBM nano compounds**

The study of DC conductivity in PPy/LBM composites is crucial for understanding charge transport mechanisms within the conducting polymer matrix and its associated dopants. In these composites, electrical conduction predominantly occurs through thermally activated hopping of charge carriers namely, polarons and bipolarons—between localized states. These carriers migrate from occupied to unoccupied sites under the influence of thermal energy, a mechanism characteristic of disordered conjugated polymer systems.The presence of LBM nanoparticles can influence this hopping behavior by introducing additional localized states, modifying the polymer’s microstructure, or facilitating charge delocalization, thereby affecting the overall conductivity. Detailed analysis of the temperature dependence of DC conductivity can thus provide insights into the charge transport dynamics and the role of nanoparticle doping.

DC conductivity of the PPy/LBM composites was measured using the standard two-probe technique. For this purpose, pelletized samples with thicknesses ranging from 1 mm to 3 mm were prepared using a hydraulic press. The flat surfaces of the pellets were coated with silver paste to ensure good electrical contact and were used as electrodes in the measurement setup. The conductivity measurements were performed at elevated temperatures using a programmable furnace set to 200 °C. Voltage readings were recorded at 5 °C intervals under a constant current condition. A Keithley source measure unit with Pico ampere scale sensitivity was employed to ensure accurate measurement of low conductivity values. The DC conductivity (σ) was calculated using the general formula:

 ……………(3)

Where R, L and A are the resistance (ohm), thickness (cm) and area (cm2) of the pellet respectively

Figure 3 presents the DC conductivity as a function of temperature for pristine PPy and PPy/LBM composites. The conductivity remains relatively constant up to 430 K, beyond which it increases markedly with temperature. This behavior is the characteristic of semiconducting materials, where thermal activation facilitates charge carrier mobility confirming thermally activated transport in both PPy/LBM systems. Comparative analysis reveals that pure PPy exhibits lower conductivity across the temperature range than its LBM-doped counterparts. The enhancement in conductivity upon LBM incorporation is primarily attributed to improved charge transport pathways and potential ionic conduction facilitated by the nanoparticles **[21–23]**. As the temperature increases, the mobility of charge carriers, including polarons and ions, becomes more pronounced, further boosting conductivity.

Among the composites, the PPy/LBM30 sample shows the highest DC conductivity, reaching a value of 0.0936 S cm⁻¹ at room temperature. This result underscores the synergistic effect of LBM nanoparticle inclusion in enhancing electrical performance and highlights the potential of these composites for thermally responsive electronic applications.



**Figure 3: DC conductivity of PPy and PPy/LBM nano composites**

**3.5. Activation energy studies of PPy, and PPy/LBM nano compounds**

Activation energy is a pivotal concept that indicates the minimum energy needed for a reaction to take place. To understand the mechanisms involved in the reaction, we can use the Arrhenius equation **[24-,27]** which connects activation energy with the reaction rate. given by

 ..............(4)

Where, K, Ea, R, and T represent the rate constant, activation energy (eV), gas constant (8.3145 J/K·mol), and temperature (K), respectively. The proportionality constant A, known as the frequency factor, is expressed in L·mol⁻¹·s⁻¹. The activation energies for the PPy, and PPy/LBM nano compounds were calculated by linear fit of the plot. The corresponding graphs are shown in figures 4(a-e).

**Figure 4.a. Linear fit of PPy/LBM10**  **4.b. Linear fit of PPy/LBM20**

**4.c. Linear fit p of PPy/LBM30 4.d. Linear fit of PPy/LBM40**



**4.d. Linear fit of PPy/LBM50**

It is evident that the figures (4a-d) activation energies for the PPy/LBM has anomaly variation in the activation energy. This result from the fact that dc conductivity is influenced by both temperature and the dielectric constant of the material **[25-27].** Compounds with a higher dielectric constant usually exhibit higher activation energies. The observed rise in activation energy can be attributed to the notable bipolaron separation band, which creates a substantial potential barrier that hinders charge carrier mobility when nanoparticles are introduced and dispersed within the host material **[28-30].** Table 2 presents the calculated activation energies for the compounds

**Table 2: Activation energy of PPy/LBM nano composites**

|  |  |
| --- | --- |
| **Compound** | **Activation energy of PPy/LBM composites in eV** |
| PPy/LBM10 | 0.083 |
| PPy/LBM20 | 0.513 |
| PPy/LBM30 | 0.443 |
| PPy/LBM40 | 0.5122 |
| PPy/LBM50 | 0.790 |

**4.Conclusions**

In this study, we investigated the optical properties of PPy/La0.7Ba0.3MnO3 nanocomposites at room temperature. The UV-IR absorption spectrum reveals a strong peak around at 327 nm and 390 nm for the composites. The energy gap decreases but not in a particular trend. This variation in the energy gap results from interatomic transitions among different energy levels, indicating transitions occurring within the same site. Overall, the incorporation of LBM nanoparticles into the PPy chain effectively modifies the optical band gap of the material. DC conductivity of PPy/LBM compound suggests the semiconductor characteristics of the composites. The increase in activation energy is due to the considerable splitting of the bipolaron. band, which creates a substantial potential hindrance to charge carrier movement when nanoparticles are introduced and dispersed within the host material. The DC conductivity study also reveals the anomaly variation with respect to LBM percentage in PPy. The study also shows that higher dielectric constant also influences the activation energy of the compound.

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