**Analysis of Optical Band Gap**, **DC Conductivity and Activation energy in Barium-Doped Lanthanum Manganite Nanoparticles tailored with PolyPyrrole**

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**Abstract:** This paper investigates the impact of incorporating La0.7Ba0.3MnO3 (LBM) perovskite nanoparticles at different weight percent ratios (10%,20%,30%,40%,50%) on DC conductivity and the optical band gap of conducting polypyrrole (PPy), synthesized via a chemical oxidation method. The morphology and crystalline structure were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Optical band gap measurements were conducted with a UV-Vis spectrometer over the range of 200 nm to 600 nm for pure PPy and PPy/LBM composites. UV-Vis spectrum shows a distinct peak around 315 nm for pure PPy and the PPy/LBM composites with 10% and 20% LBM. However, as the LBM weight percentage increased to 30%, 40%, and 50%, the peak shifted to longer wavelengths, at 320 nm, 325 nm, and 335 nm, respectively. The optical band gap increased for pure PPy, PPy/LBM10, and PPy/LBM20, while it gradually decreased for the higher LBM compositions (PPy/LBM30, PPy/LBM40, and PPy/LBM50). While DC conductivity show semiconductor behavior of the composites. 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

1. **Introduction**

Research on nanocomposites is advancing rapidly due to their wide range of applications. Among these, studies related to optical band gap have gained particular attention for their potential use in LEDs, optoelectronic devices, and energy storage systems. Wide bandgap semiconductors are especially important as they can operate efficiently at high temperatures, frequencies, and voltages. These materials typically have energy gaps between 2 eV and 4 eV, in contrast to conventional semiconductors, which possess bandgaps ranging from 0.7 eV to 1.1 eV. Doped semiconductors in this broader range are considered ideal for various applications **[1-2].**

In our research, we focus on polypyrrole (PPy), an intrinsically conducting polymer valued for its environmental stability, conductivity, mechanical strength, and optical and magnetic properties. The process involved in polymerization PPy is highly influenced by factors such as solvent choice, electrochemical conditions, concentration, doping level, and synthesis temperature, all of which affect its conductivity and optical characteristics **[3-5].**

Ceramic materials with the general formula ABO3 are also gaining attention in industrial applications, including electronics, spintronics, magnetic sensors, and energy storage. Given the broad potential of perovskite materials, we selected Barium-doped lanthanum manganite (La0.7Ca0.3MnO3) for this study. The optical bandgap of these materials is a key property influenced by their crystallinity and stoichiometry. La0.7Ca0.3MnO3 has a bandgap of 3.89 eV and an orthorhombic crystal structure **[6-7].** Leveraging the well-defined crystalline structure of this manganite, we aimed to explore its combination with polypyrrole and investigate the resulting optical transitions in the composites.

Research on PPy/LBM nanocomposites is still limited, and our study seeks to explore their optical properties. The findings could have significant implications for optoelectronics, particularly in the development of organic-based transistors, photoresistors, and organic solar cells that must perform at high voltages **[8-9].**

**Material and methods**

Material used for the compound preparation, its Synthesis procedure, the characteristics studies 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]**

**Results and Discussion**

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

To investigate the optical properties of the prepared composites, UV-Visible absorption measurements were conducted using a Cary 5000 instrument, recording data within the range of 200 nm to 1000 nm. This study has valuable insights into the interatomic transitions within the nanocomposite containing polypyrrole at room temperature.

UV-Visible-NIR spectroscopy was employed to examine the spectral absoption of PPy, pure LBM, and PPy/LBM nanocomposites. The data was taken in absorption and also in reflection modes across the 200 nm to 1000 nm range. Figure shows 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, while the peaks at 370 nm and 390 nm correspond to π-π\* transitions happening inside the benzoid ring **[12].**



Figure 1. Spectral absorbance PPy/LBM composites

**1.2 Optical band gap measurements**

Figure 2.a displays the absorbance spectra for LBM, PPy, PPy/LBM10, PPy/LBM30, and PPy/LBM50. A peak at 278 nm, commonly observed across the composites, is attributed to the absorption of spectral energy by water molecules that may be present. The main absorption peak for pure LBM occurs around 326 nm, while pure PPy exhibits a characteristic peak at 338 nm. For the PPy/LBM10 composite, a peak at 339 nm is associated with weaker π-π\* transitions within PPy, likely due to the formation of polarons **[13-14].** The band gaps of the PPy/LBM nanocomposites were determined using the K-M plot based on the reflectance data. The energy band gaps for the PPy/LBM nanocomposites are presented in Figure 2 (a-e).

 

 



Figure. 2: Optical band gap: a. PPy/LBM10, b. PPy/LBM20, c. PPy/LBM30

d. PPy/LBM40, e. PPy/LBM50

PPy/LBM50, two absorption peaks are noted at 327 nm and 340 nm, where the former corresponds to weak polaron transitions and the latter to bipolaron transitions, which arise from the increased filler content of LBM. This suggests a strong interaction allying PPy and the LBM nanoparticles, enhancing the polymer chain formation through effective monomer linking.

Additionally, PPy/LBM composites (10% and 50% by weight) show slight shifts in peak positions, indicating that LBM nanoparticles has significant effect on the optical spectral absorption wavelengths of the PPy chain. A long tail extending on the outside of 400 nm to 1000 nm is also observed in all composites, likely due to defects or impurities present during synthesis. Overall, the peaks noticed in the absorbance spectra confirm that the composites exhibit good optical absorption in the range of 250 nm to 350 nm **[15]**, which may be advantageous for applications in nonlinear frequency conversion.

**1.3. 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 (PPy) 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 **[16-17].** The optical band gap is commonly analyzed using Tauc's plot, 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

One key observation is that the optical band gap of PPy is larger than that of the PPy/LBM nanocomposites. However, the incorporation of LBM nanoparticles into the PPy chain results in a slight variation in the band gap. Table 1 illustrates the variation in the band gap with different percentages of LBM in PPy. This change in band gap is attributed to the quantum mechanical effect known as quantum confinement. The transition occurs between the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the constituent conjugated polymer (PPy) and the dopant (LBM nanoparticles). The observed change in the band gap compared to pure PPy indicates an interaction between PPy and the LBM nanoparticles.

Table 1. Optical Band gap of PPy/LBM

nano composites

|  |  |
| --- | --- |
| **Name of the compound** | **Optical band gap (eV)** |
| PPy | 3.11 |
| PPy/LBM10 | 3.09 |
| PPy/LBM20 | 3.01 |
| PPy/LBM30 | 3.14 |
| PPy/LBM40 | 3.12 |
| PPy/LBM50 | 3.08 |

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

The study of DC conductivity in the composites is essential as it pertains to the movement of charge carriers within the conducting polymer and its dopants. Conduction typically occurs through the hopping of polarons and bipolarons from occupied to vacant sites, driven by thermal energy.

In this work, DC conductivity was measured using a two-probe method. Pelletized samples, with thicknesses ranging from 1 mm to 3 mm, were prepared. The pellets were made as electrodes for the study by applying silver paste . Measurements were taken at a furnace temperature of 200 °C, with voltage recorded at 5 °C intervals while maintaining a constant current. A Keithley apparatus with pico-scale sensitivity was used for the measurements. The general equation for DC conductivity is given by:

 ……………(3)

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

Figure 3 shows the plots of DC conductivity as a function of temperature for PPy and PPy/LBM composites. It is clear from the figure that the measured conductivity remains steady up to 430 K, after which it increases significantly. This trend suggests DC conductivity and the temperature varied has inverse relation, confirming that both PPy and PPy/LBM nanocomposites exhibit semiconducting behavior. Upon comparison, pure PPy demonstrates lower conductivity than the PPy/LBM composites **[18-20]**. The presence of LBM nanoparticles in these composites enhances electrical conduction, primarily through ionic conduction, which improves with increasing temperature. Notably, the PPy/LBM30 nanocomposites show a high DC conductivity value of 0.0936 S cm⁻¹ at room temperature.



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

**1.5. 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, 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.

 

 



Figure 4. Linear fit :a. PPy/LBM10, b. PPy/LBM20, c. PPy/LBM30

d. PPy/LBM40, e. PPy/LBM50

Table 2 presents the calculated activation energies for the compounds. It is evident that the activation energies for the PPy/LBM samples are higher compared to pure PPy. While an increase in LBM content typically leads to higher activation energies, this trend was not observed in this case. This anomaly could result from the fact that dc conductivity is influenced by both temperature and the dielectric constant of the material. 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. **[21].**

Table 2: Activation energy of PPy/LBM nano composites

|  |  |
| --- | --- |
| **Compound** | **Activation energy of PPy/LBM composites in eV** |
| Pure PPy | 0.0991 |
| PPy/LBM10 | 0.083 |
| PPy/LBM20 | 0.513 |
| PPy/LBM30 | 0.443 |
| PPy/LBM40 | 0.5122 |
| PPy/LBM50 | 0.790 |

**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 340 nm the composites. The energy gap decreases various 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. These findings suggest potential applications in organic optoelectronic devices that operate at high voltages. 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.

**References**

1.Xinbo Ma, Zhenyu L, “The Important Role of Optical Absorption in Determining the Efficiency of Intermediate Band Solar Cells and a Design Principle for Perovskite Doping”, J. Phys. Chem. Lett. 2022, 13, 8.

2.Xinbo Ma, Wenjun Chu, Youxi Wang, Zhenyu Li, Jinlong Yang, “Increasing the Efficiency of Photocatalytic Water Splitting via Introducing Intermediate Bands”, J. Phys. Chem. Lett 2023, 14 (3), 779-784.

3.Md. Helal MiahORCID logoab, Mayeen Uddin Khandaker, Md. Bulu Rahmanb, Mohammad Nur-E-Alamde and Mohammad Aminul Islamf, “Band gap tuning of perovskite solar cells for enhancing the efficiency and stability: issues and prospects”, RSC Adv., 2024, 14, 15876-15906.

4.Constantinos C. Stoumpos, Duyen H. Cao, Daniel J. Clark, Joshua Young, James M. Rondinelli,Joon, I. Jang Joseph, T. Hupp Mercouri G. Kanatzidis, “Ruddlesden-Popper Hybrid Lead Iodide Perovskite 2D Homologous Semiconductors”, Chem. Mater., 2016, 28(8), 2852–2867.

5.Zhenhua Yang, Yichen Guo, Hongfei Li, Yuchen Zhou, Xianghao Zuo, Yingjie Yu, Cheng Pan, Joseph Strzalka, Chang-Yong Nam, Miriam H. Rafailovich, “Roles of Interfacial Tension in Regulating Internal Organization of Low Bandgap Polymer Bulk Heterojunction Solar Cells by Polymer Additives”, Adv. Mater.Interfaces,2018,5,15

6.Keller Andrews, Anthony B. Kaye, “Optimized procedure for sol–gel production of La2/3Ca1/3MnO3 thin films”, J.SST, 2015,76, 372–377.

7.S.O. Manjunatha, A. Rao, G.S. Okram, “Investigation on structural, magneto-transport, magnetic and thermal properties of La0.8Ca0.2−xBaxMnO3 (0 ≤ x ≤ 0.2) manganites”. J. Alloys Compd. 2015,640, 154–161.

8.H. Eisazadeh, “Studying the characteristics of polypyrrole and its composites”. World J. Chem.2007, 2(2), 67–74.

9.B. Kurniawan, S. Winarsih, C. Kurniawan, M. R. Ramadhan, and F. Ruli, “The effect of Ca-doping on structure and microstructure of La0.7(Ba1-xCax)0.3MnO3”. In: AIP Conference Proceedings , 2017,1862, 030054. https://doi.org/10.1063/1.4991158.

10.Smitha M G, Murugendrappa M V, “Effect of barium lanthanum manganite nano particle on the electric transport properties of polypyrrole at room temperature”, J. Mater.Electron, 2019, 30(4).

11. Smitha M G, Shwetha, Polypyrrole/lanthanum manganite: A comparative study of morphology, Structural, VSM, and EPR studies, Futuristic Trends in Chemical, Material Sciences & Nano Technology, IIP Series, Volume 3, Book 1, Chapter 22.

12. Liuxu Yu, Mingyuan Wang, Haigang Hou, Xiangzhao Zhang, Shuangying Lei, Junlin Liu, Guiwu Liu, Guanjun Qiao, “Enhanced optical properties and mechanisms of Ba-doped LaMnO3 perovskite ceramic coating”, Ceram.Int.2023, 49, 7, 11696-11704.

13. Rifei Han, Naeem ul Haq Tariq,Feng Zhao, Lijia Zhao, Housheng Liu , Jiqiang Wang Xinyu Cui, Tianying Xiong, “High infrared emissivity energy-saving coatings based on LaMnO3 perovskite ceramics”, Ceram.Int.2022,48,14, 20110-20115.

14. Moustafa Tawfik Ahmed, M. T. Ahmed, M. I. Abdel Hamid, A. Sarhan,A. A.Ali “Synthesis and Structural Characterization of Polypyrrole (PPy) - Chitosan (Cs) Nanocomposite: Influence of UV Irradiation”,Global Journal of Physics 2018,7,1.

15. Andreja Žužić, Antonia Ressler, Ana Šantić, Jelena Macan, Andreja Gajović, “The effect of synthesis method on oxygen nonstoichiometry and electrical conductivity of Sr-doped lanthanum manganites”,2022, J.Alloys Compd.907,25,  164456.

16. Andreja Žužić , Luka Pavić, Arijeta Bafti, Sara Marijan, Jelena Macan , Andreja Gajović ,” The role of the A-site cation and crystal structure on the electrical conductivity of strontium-doped calcium and barium manganites”,2023, J.Alloys Compd,935, 167949.

17. Toribio F. Otero & Jose G. Martinez, “Activation energy for polypyrrole oxidation: film thickness influence”, 2011, J.Solid State Electr,15, 1169–1178.

18. Basavaraja Patel B M, M Revanasiddappa, D R Rangaswamy, S Manjunatha and Y T Ravikiran, “DC conductivity studies of iron decorated polypyrrole”,2021, J. Phys.: Conf. Ser. 2070 012070.

19. Megha R, Ravikiran Y T, Vijayakumari S C, Rajprakash H G, Revanasiddappa M, Manjunatha S, Thomas S, “AC conductivity studies in copper decorated and zinc oxide embedded polypyrrole composite nanorods: Interfacial effects”, J.Mater. Sci.: Mater. Electron, 2020, 110, 104963.

20. Wided Hizi, M. Wali, H. Rahmouni, K. Khirouni & E. Dhahri, “Examination of charge-carriers hopping and identification of relaxation phenomenon and blocking effect in perovskite system”, Eur.Phys.J. Plus,2024, 139,156.

21. M.D. Migahed, T. Fahmy, M. Ishra, A. Barakat, “Preparation, characterization, and electrical conductivity of polypyrrole composite films”, Polym.Test, 2004, 23, 3, May 2004, 361-365.