Structural and Optical Properties of Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI Nanocomposites

Shaweta Sharma$^1$, J. Mohammed$^1$, Tchouank Tekou Carol Trudel$^1$, R.S Getso$^1$, Pushpendra Kumar$^2$, D. Basandrai$^1$, A. K. Srivastava$^1$,*

$^1$Department of Physics, Lovely Professional University, Phagwara-144411, Punjab, India

$^2$Department of Chemistry, Lovely Professional University, Phagwara-144411, Punjab, India

*Corresponding author: srivastava_phy@yahoo.co.in

Abstract. Recently Hexaferrites have attracted the attention of researchers due to its wide applications such as permanent magnets, magnetic recording media, microwave applications and Wireless telecommunication system. Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$ was successfully synthesized using sol-gel method while oxidative polymerization was employed to synthesized polyaniline (PANI). The precursor material is pre sintered at 500°C for 5 hours and sintered at 1000°C for 5 hours. The characteristics of the samples were defined by using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and Ultraviolet visible spectrophotometer (UV-vis). XRD analysis confirms the spectral purity of the sample. FTIR analysis indicates the formation of y-type hexaferrites by the appearance of two prominent peaks at 400 and 600 cm$^{-1}$. Raman spectra show the presence of Y-type hexaferrites and PANI by the appearance of prominent Raman shifts. The band gap of the prepared nanocomposites was evaluated using UV-vis spectroscopy.

Keywords: Y-type hexaferrites, PANI, Oxidative polymerization, Sol-gel method

1. INTRODUCTION

Hexaferrites are discovered in 1950 [1] have received the curiosity of researchers because of their brilliant magnetic properties which make them capable for applications such as magnetic recording media, magnetic storage, RAM, aircraft(stealth technology)[2] Hexagonal ferrites are splits into six types in accordance with their chemical composition and crystalline structure they are M-type (BaFe$_{12}$O$_{19}$), Y-type (Ba$_2$Me$_2$Fe$_{12}$O$_{22}$), U-type (Ba$_4$Me$_2$Fe$_{36}$O$_{60}$), W-type (BaMe$_2$Fe$_{16}$O$_{27}$), X-type (Ba$_3$Me$_2$Fe$_{28}$O$_{46}$) and Z-type (Ba$_3$Me$_2$Fe$_{26}$O$_{41}$). General formula of Y-type hexaferrites is A$_2$Me$_2$Fe$_{12}$O$_{22}$ (A= Ba$^{2+}$, Sr$^{2+}$, Me= divalent metal ions such as Ni, Zn, Co. Y-type Hexaferites are a useful combination of ferromagnetic and isolating properties and are also known for their use as magneto- electrical devices. Especially in Y-type
hexaferrites, the spins in the basal plane have been observed to be collinear. The Y-type hexaferrites structure has space group (R3m) [3] [4]. Researcher has paid close attention to the composite of ferrites with conductive polymers due to their electric and ferromagnetic properties [5]. Among all the conducting polymers, polyaniline (PANI) is considered a promising material due to their low density, easy preparation, having good stability and widely used for electronic and optical applications [6].

Several methods have been used for the synthesis for Y-type hexaferrites such as melting method, ceramic method, solid-state reaction method, citrate precursor method, co-precipitation, hydrothermal methods, crystallization method, ball milling method, microemulsion technique so on but these methods have disadvantages alike high calcination temperature, non-homogeneity of particles. In this work, Sol-Gel auto combustion technique is used for Y-type hexaferrites because this method shows several advantages include low processing cost, lower calcination temperature, and energy efficient, good homogeneity of particles [7]. Polyaniline (PANI) was synthesized via Oxidative Polymerization method [8].

2. EXPERIMENTAL METHODS

2.1 MATERIAL AND METHODS

Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI nanocomposites were synthesized by different weight ratios Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI (1, 1:0.5, 1:1). Y-type hexaferrites was prepared by using Sol-Gel auto combustion method at room temperature. The adding materials were Sr(NO$_3$) were dissolved in 100ml of distilled water in a 500ml beaker according to their stoichiometric ratios. In order to ensure the citric acid molar ratio is 1:1.5, citric acid has been added. The ammonia solution was subsequently added dropwise to retain the pH of 7.0. This solution was then put on a magnetic stirrer with continuous stirring at a temperature of 80$^\circ$C to 85$^\circ$C for 3-4 hours in order to evaporate the liquid and produce the viscous brown gel. This gel was then placed for 1 hour on a hot plate at 250$^\circ$C-300$^\circ$C to extract the water and obtain the powdered precursor material. This precursor material was then heated for 6 hours at 1100$^\circ$C to obtain Y-type hexaferrites.

Polyaniline (PANI) was synthesized by oxidative polymerization method. In an ice bath at 0$^\circ$C, 23.28 gm of aniline monomer was slowly poured into 91.15ml of hydrochloric acid (HCL). The solution was allowed to stirrer for 1 hour. After that add 40.47 gm of Ammonium sulphate dissolve in water in the above HCL solution and allowed to stirred for 1 hour. After that with distilled water, the solution was filtered and washed. The specimen was dried for 48 hours in an oven at 60$^\circ$C.

2.2 Synthesis of Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI nanocomposites

Above powdered samples were mixed in a mortar and pestle by mechanical grinding to make the powder homogenous. The ratio of polyaniline was varied from one sample to another (1, 1:0.5, 1:1). The sample code of the nanocomposite is given

Table 1. Shows the sample code of Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI.

| Sample Code | Ratio |
|-------------|-------|
| YP1         | 1:0   |
3. RESULTS AND DISCUSSIONS

3.1. XRD Analysis

XRD pattern in the range of 20-80° was observed. The observed diffraction peaks were indexed to standard JCPDS 440206 and the presence of Y-type hexaferrites was found. According to the JCPDS, the diffraction peaks are at (119), (024), (205), (016), (0219), (033), (1025), (0214), (0027), (0126), (0315) hkl planes of Sr hexaferrites. But the presence of PANI was not observed. The lattice parameter (a,c), Volume of unit cell (V_cell) and Crystalline size(D) were calculated using following relations.

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + hk + l^2}{a^2} \right)
\]

\[D = \frac{k\lambda}{\beta \cos \theta}\]

\[V_{cell} = 0.8666a^2c\]

Where \(d_{hkl}\) Dspacing, hkl are the miller indices, \(\theta\) is a braggs angle. \(k=1\), shape factor for hexaferrites, \(\lambda=1.54056\) is the X-ray Wavelength \(\beta\) (in rad) is the full width half maxima

| YP2  | 1:0.5 |
|------|-------|
| YP3  | 1:1   |

Fig 1. XRD pattern for \(\text{Sr}_2\text{Co}_{1.0}\text{Bi}_{0.1}\text{Fe}_{11.9}\text{Zn}_{0.1}\text{O}_{22}/\text{PANI}\)
Table 2. Shows the value of lattice constants (a, c), Crystalline size D(nm) and Volume of cell (Vcell).

| Sample code | 2(\theta) (degree) | dhkl (Å) | \(\beta\) (rad) | a (Å)  | c (Å)  | D(nm)  | Vcell (Å³) |
|-------------|---------------------|----------|-----------------|-------|-------|--------|-----------|
| YP1         | 30.37               | 2.9410   | 0.371           | 5.882 | 43.01 | 24.66  | 1289.56   |
| YP2         | 30.38               | 2.9396   | 0.144           | 5.8792| 43.02 | 63.52  | 1288.62   |
| YP3         | 30.43               | 2.9356   | 0.175           | 5.8712| 43.11 | 52.27  | 1287.80   |

### 3.2 FTIR Analysis

The FTIR spectra of Sr₂Co₁.₉Bi₀.₁Fe₁₁.₉Zn₀.₁O₂₂/PANI is shown in figure. There are two peaks observed at 437 cm⁻¹ and 585 cm⁻¹. The peaks appear between 400 cm⁻¹ and 600 cm⁻¹ indicates the presence of ferrites due to the metal-oxygen bond vibration [9]. The peak observed at 1074 cm⁻¹ is due to the vibrational mode of NQN, where Q refers to the quionoid rings that confirms the presence of polyaniline in composite [10]. The peak at 2354 cm⁻¹ is due to the CO₂ absorbed from the atmosphere by the sample [11].

![FTIR pattern](image)

Fig 2. FTIR pattern for Sr₂Co₁.₉Bi₀.₁Fe₁₁.₉Zn₀.₁O₂₂/PANI.
3.3 Raman Analysis

Figure 3 shows the Raman spectra of Y-type/PANI nanocomposites at room temperature recorded in the range of 0-2500 cm\(^{-1}\). According to our knowledge, we noticed that there is very less research has been done on the raman spectra of Y-type hexaferrites. Peaks under the range from 500-700 cm\(^{-1}\) confirms the existence of Y-type hexaferrites \[12\]. Peaks between 1100–1600 cm\(^{-1}\) shows the presence of PANI, which is not given by XRD. Peak between 1100-1200 cm\(^{-1}\) is assign to the vibration of CH stretching of the quinoid group. Peak between 1300-1400 cm\(^{-1}\) is assign to the vibration of CN stretching of the benzenoid ring. Peak between 1500-1600 cm\(^{-1}\) is assign to the semi quinone cation structure of Polyaniline\[13\].

![Raman Spectra of Sr\(_2\)Co\(_{1.9}\)Bi\(_{0.1}\)Fe\(_{11.9}\)Zn\(_{0.1}\)O\(_{22}\)/PANI.](image)

3.4. UV analysis

UV visible spectra of of Sr\(_2\)Co\(_{1.9}\)Bi\(_{0.1}\)Fe\(_{11.9}\)Zn\(_{0.1}\)O\(_{22}\)/PANI was shown in figure Y-type/PANI nanocomposites peak was observed between 200-300 nm is due to the exciton absorption of quinoid rings as well as the \(\pi\) to \(\pi^*\) transitions of benzenoid rings. Optical band gap was also calculated in this Spectra. Usually the optical band gap has to be decreased with the addition of PANI in hexaferrite but the opposite trend is observed in this that as we add PANI the band gap decreased, same type of behaviour was observed by A.I Nandapure \[14\]. The observed band gap of Y-type hexaferrite was 3.4eV, as we add PANI the optical band gap increased that is the optical band gap of PANI is 4.72eV (1:0.5). By increasing the concentration of PANI in the nanocomposite band gap decreased 4.71eV (1:1).
Fig 4. UV spectra of Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI.

4. Conclusion

The presence of Sr$_2$Co$_{1.9}$Bi$_{0.1}$Fe$_{11.9}$Zn$_{0.1}$O$_{22}$/PANI nanocomposites was confirmed by FTIR and Raman. FTIR study shows the presence of PANI at 1074 cm$^{-1}$. Raman spectroscopy shows the presence of PANI between 1100-1600 cm$^{-1}$. UV study shows that with the increased in the concentration of PANI in the nanocomposites the optical band gap decreased, which make nanocomposite most suitable candidate for electronic devices and high frequency applications.

REFERENCES

[1] R. C. Pullar, “Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics,” *Prog. Mater. Sci.*, vol. 57, no. 7, pp. 1191–1334, 2012.

[2] R. C. Pullar, S. G. Appleton, and A. K. Bhattacharya, “The microwave properties of aligned hexagonal ferrite fibers,” *J. Mater. Sci. Lett.*, vol. 17, no. 12, pp. 973–975, 1998.

[3] Y. Bai, J. Zhou, Z. Gui, Z. Yue, and L. Li, “Complex Y-type hexagonal ferrites: An ideal material for high-frequency chip magnetic components,” *J. Magn. Magn. Mater.*, vol. 264, no. 1, pp. 44–49, 2003.
[4] M. Y. Salunkhe and D. K. Kulkarni, “Structural, magnetic and microstructural study of Sr2Ni 2Fe12O22,” J. Magn. Magn. Mater., vol. 279, no. 1, pp. 64–68, 2004.

[5] N. N. Ali, R. Al-Qassar Bani Al-Marjeh, Y. Atassi, A. Salloum, A. Malki, and M. Jafarian, “Design of lightweight broadband microwave absorbers in the X-band based on (polyaniline/MnNiZn ferrite) nanocomposites,” J. Magn. Magn. Mater., vol. 453, pp. 53–61, 2018.

[6] T. Ben Ghzaiel, W. Dhaoui, F. Schoenstein, P. Talbot, and F. Mazaleyrat, “Substitution effect of Me = Al, Bi, Cr and Mn to the microwave properties of polyaniline/BaMeFe 11 O 19 for absorbing electromagnetic waves,” J. Alloys Compd., vol. 692, pp. 774–786, 2017.

[7] M. Ahmadipour, M. F. Ain, and Z. A. Ahmad, “A Short Review on Copper Calcium Titane (CCTO) Electroceramic: Synthesis, Dielectric Properties, Film Deposition, and Sensing Application,” Nano-Micro Lett., vol. 8, no. 4, pp. 291–311, 2016.

[8] A. I. Nandapure, S. B. Kondawar, B. I. Nandapure, and M. M. Choudhari, “Structural and optical properties of polyaniline/nickel ferritenanocomposites,” Adv. Mater. Proc., vol. 2, no. 7, pp. 463–467, 2017.

[9] T. T. Carol Trudel, J. Mohammed, H. Y. Hafeez, B. H. Bhat, S. K. Godara, and A. K. Srivastava, “Structural, Dielectric, and Magneto-Optical Properties of Al-Cr Substituted M-Type Barium Hexaferrite,” Phys. Status Solidi Appl. Mater. Sci., vol. 1800928, pp. 1–9, 2019.

[10] Y. He, “Synthesis of polyaniline/nano-CeO2 composite microspheres via a solid-stabilized emulsion route,” Mater. Chem. Phys., vol. 92, no. 1, pp. 134–137, 2005.

[11] J. Mohammed et al., “Lightweight SrM/CCTO/rGO nanocomposites for optoelectronics and K u band microwave absorption,” J. Mater. Sci. Mater. Electron., vol. 30, no. 4, pp. 4026–4040, 2019.

[12] H. Khanduri et al., “Structural, dielectric, magnetic, and nuclear magnetic resonance studies of multiferroic Y-type hexaferrites,” J. Appl. Phys., vol. 112, no. 7, 2012.

[13] J. Luo, Y. Zuo, P. Shen, Z. Yan, and K. Zhang, “Excellent microwaveabsorption properties by tuned electromagnetic parameters in polyaniline-coated Ba0.9La0.1Fe11.9Ni0.1O19/reduced graphene oxide nanocomposites,” RSC Adv., vol. 7, no. 58, pp. 36433–36443, 2017.

[14] A. I. Nandapure, P. S. Sawadh, S. B. Kondawar, and B. I. Nandapure, “Synthesis and characterization of zinc ferrite - polyaniline nanocomposites,” Int. J. Adv. Sci. Tech. Res., vol. 5, no. 5, pp. 82–89, 2015.