Structural and Optical Properties of $\text{Ba}_{0.7}\text{Dy}_{0.3}\text{Fe}_{11.4}\text{Cr}_{0.6}\text{O}_{19}$/Polyaniline (PANI) Nanocomposites for Optoelectronics

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Abstract

M-type hexaferrites have found considerable application in microwave absorption and magnetic recording. Sol-gel auto-combustion technique was utilized to prepare $\text{Ba}_{0.7}\text{Dy}_{0.3}\text{Fe}_{11.4}\text{Cr}_{0.6}\text{O}_{19}$ nano-sized particles which were sintered at 1000 °C for 6 hours. XRD patterns of the prepared sample show magnetoplumbite phase of M-type hexaferrite along with the presence of hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) and polyaniline. Two specific bands in the range 400-600 cm$^{-1}$ were observed in the FTIR spectra signifying the formation of hexaferrites structure. The peaks corresponding to polyaniline are also present in the FTIR spectra in the range 800-1600 cm$^{-1}$. FESEM analysis shows grains with shape similar to hexagonal plate embedded on the surface of polyaniline. The band gap was found to decrease from 1.96 eV to 1.59 eV.

Keywords: M-type hexaferrite, polyaniline, absorbance, band-gap

1. Introduction

The hexaferrite materials discovered in 1950 [1] have retained considerable attention due to their good magnetic properties. The big family of hexaferrite materials contains 6 types such as M, Y, W, U, X and Z which have $P63/mmc$ as space group. Especially M-type hexagonal ferrite has a large intrinsic magnetic anisotropy field [2], high value of Curie temperature (Tc= 502°C), large coercive field of 6700Oe and large saturation magnetization of 72 emu/g [3]. This material is suitable for many applications such as channel filters, printers, calculators, mobile phones, paints for microwave absorbing, IT applications,
magnetic recording, gyromagnetic devices, refrigerator magnets, medicine, magneto optical recording and supercapacitors [4-7]. Out of their dielectric and magnetic properties, optical properties of M-type hexaferrites were also studied by several authors and band gap value of BaFe$_{12}$O$_{19}$ was found to be 2.32 eV [8-12]. Several methods including Solid state reaction technique, glass crystallization method, melting method, co-precipitation method, citrate precursor method and sol-gel method have been used to prepare M-type hexaferrite materials [13-18].

Conducting polymers like polyaniline(PANI) have retained great attention due to their applications in different fields such as electrical, electronic, electromagnetic, sensors, antistatic coatings, rechargeable batteries, corrosion inhibitors and EMI shielding [2, 19]. Moreover, among conducting polymers, PANI is most used to synthesize nanocomposite materials because of their easy synthesis, low cost, tunable properties and stability. PANI is obtained by polymerizing aniline. Many types of polymerization can be used to synthesize PANI including Emulsion polymerization, enzymatic polymerization, photochemical polymerization, oxidative polymerization and autocatalytic polymerization. Among these methods, oxidative polymerization is most used because it permits to obtain a stable PANI.

In this work, sol-gel method and oxidative polymerization were used to synthesize Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$ and PANI respectively. Structural and optical properties of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI were studied.

2. Experimental method

2.1 Synthesis method of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$

Dy-Cr substituted M-type hexaferrite (Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$) was synthesized by the use of sol-gel autocombustion technique. The used raw chemicals with high purity (99-99.5%) from Loba Chemie company including Ba(NO$_3$)$_2$, Fe(NO$_3$)$_3$.9H$_2$O, Dy(NO$_3$)$_3$.9H$_2$O, Cr(NO$_3$)$_3$.9H$_2$O, ethylene glycol) and citric acid (C$_6$H$_8$O$_7$.H$_2$O) were utilized as reagents. First of all, reagents were dissolved in ethylene glycol used as solvent. Citric acid (with 1:1.5 molar ratios of cations to citric acid) was added. Then aqueous ammonia solution (NH$_4$OH) was poured dropwise to adjust the pH of the solution to 7.0. The obtained mixture was heated at around 85-100°C on a magnetic stirrer containing heating. After around 3 hours, a gel solution was obtained which was brought to around 350°C to evaporate the remaining water in the sample and precursor material was formed. The precursor material was put inside the furnace for a temperature of 1000°C for 6 hours to obtain the hexaferrite powder.

2.2 Synthesis method of polyaniline (PANI)

PANI was obtained by polymerizing aniline with ammonium persulphate (APS) as oxidant. In the procedure, some amount of concentrated hydrochloric acid (HCl) was stirring at low temperature (0-2°C) in an ice bath. Then aniline monomer was added drop by drop. After 30 min dissolved APS in water was added as well. The resulting solution was left in rotation for 1 hour and then, distilled water was added to reduce the concentration of HCl. Distilled water and methanol were used to wash the resulting solution, and then we proceeded to filtration. An oven was used to dry the sample at 60 °C for 2 days. Finally, the PANI was obtained with the color green.

2.3 Synthesis method of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composite
The powders obtained from these two previous methods were mixed in a mortar with a pestle using a mechanical grinding method. Indeed, the amount of polyaniline was varied from one sample to another according to the ratios 1: 1, 1: 2 and 1: 3 (hexaferrite: PANI) (Table 1).

| Sample code | Ratio |
|-------------|-------|
| HP11        | 1:1   |
| HP22        | 1:2   |
| HP33        | 1:3   |

3. Characterization techniques

Different phases and structural analysis of prepared samples were identified using Cu-Kα radiation in the range 20°-80° operating at 35 mA and 40 kV with step size 0.02° (Bruker AXS D8 advance diffractometer) was used for structural and phase analysis of prepared samples. FTIR spectrometer (Nicolet FTIR interferometer IR prestige-21(model-8400S)) in the range 4000-400 cm⁻¹ was used to carry out different functional groups and characteristic signature of the prepared samples. Morphology and elemental analysis of the prepared samples were examined using FESEM and EDXS (FEI Nova NanoSEM 450 FESEM). Band gap energies of those samples were carried out using UV-Vis-NIR Spectrometer (Varian, Cary 5000) in the wavelength range 200-780 nm.

4. Results and discussions

4.1 Structural analysis

X-ray diffraction patterns were used to carry out the structural properties of nanocomposites consisted by Ba₀.₇Dy₀.₃Fe₁₁.₄Cr₀.₆O₁₉/PANI. Figure 1 exhibits the XRD patterns of prepared sample. The M-type hexaferrite peaks in this figure were indexed using 39-1433 as JCPDS number [20]. The diffraction angles 23.49, 30.35, 30.79, 34.13, 35.61, 37.09, 40.35, 54.03, 55.07, 56.51, 57.55, 62.41, 63.07, 63.93, 71.88 and 75.40 corresponds to the (006), (110), (008, (107), (114), (108), (203), (205), (300), (0014), (2011), (218), (1015), (220), (0016), (2113) and (403) diffraction planes of magnetoplumbite structure with space group P6₃/mmc respectively. Moreover, the presence of second phase (α-Fe₂O₃) can be observed and was indexed using 33-0664 as JCPDS card [21]. The diffraction planes (012), (104), (024) and (018) observed at 2θ=24.14, 33.13, 49.42 and 57.54 indicate the presence of impurity which may be due to the fact that the heating time and sintering temperature of Ba₀.₇Dy₀.₃Fe₁₁.₄Cr₀.₆O₁₉ were not enough. The peak at around 2θ=25.37 indicates the presence of PANI in the composite; this observation was also reported by C. L. Yuan and J. Luo [22, 23].

Crystallite size (D), lattice constants (a and c) and volume of unit cell (V) have been calculated according to following formulae and values are tabulated in Table 2 [24, 25]

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

\[
V_{cell} = \frac{\sqrt{\tau}}{2} a^2 c
\]
where, $d_{hkl}$ represents the distance between two consecutive planes, $hkl$ represent the diffraction plane, $\beta$ is full width at half maxima (in radian), $\lambda (1.54056 \text{ Å})$ is wavelength of incident X-ray , $\theta$ is angle of deviation. The average crystallite size of prepared composite was calculated from the highest intensity peak and was found to be between 77 and 92 nm. The obtained values of $a$ and $c$ were found to be in accordance with the literature [26]. From Table 2, it can be observed that $c$ remains almost constant while a slight increase in $a$ and $V$ was observed which appears as a result of adding of PANI i.e. $a$ and $V$ increase with the increase in PANI amount. In fact, after adding PANI, the crystal structure of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$ has undergone some distortions.

![XRD patterns of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composite](image)

**Figure 1.** XRD patterns of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composite
Table 2 Crystallite size ($D$), lattice parameters ($a$ and $c$) and volume of unit cell ($V$) of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$ in prepared composite

| Sample code | Peak | $2\theta$ ($^\circ$) | $\beta$ ($^\circ$) | d-spacing | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $D$ (nm) |
|-------------|------|----------------------|-------------------|------------|----------|----------|------------|---------|
| HP11        | (300)| 54.03                | 0.104             | 1.6959     | 5.8748   | 23.2768  | 695.7218   | 85.7408 |
| HP22        | (300)| 54.02                | 0.097             | 1.6962     | 5.8758   | 23.28    | 696.0637   | 91.9242 |
| HP33        | (300)| 53.84                | 0.115             | 1.7013     | 5.8935   | 23.2736  | 700.0632   | 77.4741 |

4.2 Fourier transform-infrared (FTIR) analysis

To identify the different functional groups in the sample, FTIR spectroscopy has been used. Before FTIR analysis, some amount of the prepared sample has to be mixed with potassium bromide (KBr) in the ratio 1:10.

Figure 2. FTIR spectra of (a) PANI, (b) HP11, (c) HP22 and (d)HP33
Then the mixture powder was transformed into pellet using KBr press. FTIR spectra were recorded between 400 and 4000 cm\(^{-1}\). **Figure 2** shows FTIR spectra for polyaniline (PANI) and Ba\(_{0.7}\)Dy\(_{0.3}\)Fe\(_{11.4}\)Cr\(_{0.6}\)O\(_{19}\)/PANI composites in the range 400-4000 cm\(^{-1}\). In all FTIR spectra, PANI peaks can be observed in the range 800-1600 cm\(^{-1}\). At around 1567 cm\(^{-1}\) and 1486 cm\(^{-1}\)the observed peaks are assigned to C=C stretching vibration of quinoid and benzenoid rings. Absorption bands at 1306 cm\(^{-1}\) and 1253 cm\(^{-1}\) are assigned to N-H bending and asymmetric C-N stretching modes of the benzenoid ring whereas the peak at 1142 cm\(^{-1}\) correspond to vibrational modes of N=Q=N (Q represents quinonic ring). The C-H out plane vibration of benzene ring is observed at around 804 cm\(^{-1}\) [2, 22, 27, 28]. Two important peaks are observed at around 437 cm\(^{-1}\) and 590 cm\(^{-1}\) indicating the formation of hexaferrite [20]. These bands refer to the vibration of ferric crystallographic site. The large absorption peak with weak intensity observed between 3200-3600 cm\(^{-1}\) in composites is assigned to the presence of hydroxyl (OH) groups. At around 2360 cm\(^{-1}\), the presence of CO\(_2\) absorbed from atmosphere in the composite. It can be noticed that the intensity of peaks between 400 and 600 cm\(^{-1}\) gradually decrease, this may be a consequence of the strong presence of PANI in the composite.

4.3 Morphological analysis

**Figure 3(a)** shows FESEM micrographs of Ba\(_{0.7}\)Dy\(_{0.3}\)Fe\(_{11.4}\)Cr\(_{0.6}\)O\(_{19}\)/PANI composite. It can be well observed that all hexagonal particles are coated indicating the presence of PANI. It was observed that particles exhibit a homogeneous distribution. Imagej software was used to estimate the average particles size of prepared composite and it was found to be 0.311\(\mu\)m (**Figure 3(b)**). It can be noticed that the average particle size obtained from FESEM is greater than the crystallite size of Ba\(_{0.7}\)Dy\(_{0.3}\)Fe\(_{11.4}\)Cr\(_{0.6}\)O\(_{19}\) obtained from XRD analysis. Indeed, a particle is generally composed of one or more than one crystallite. Moreover, the fact that the Ba\(_{0.7}\)Dy\(_{0.3}\)Fe\(_{11.4}\)Cr\(_{0.6}\)O\(_{19}\) and \(\alpha\)-Fe\(_2\)O\(_3\) particles are coated with PANI also increases the size of particle. **Figure 4** presents EDX spectra of prepared composite. From this figure, all the substituted and host present in the prepared samples can be observed with their corresponding weight percent. This confirms the formation of hexaferrite and PANI revealed by XRD analysis.

![Figure 3](image-url)
4.4 Optical analysis

Optical properties of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composite were carried out using UV-visible absorption spectra. Figure 5 shows absorption spectra of prepared sample in the range 200-800 nm. J. Deng and P. K. Khanna have reported that PANI shows two large absorption bands in UV-vis spectroscopy at around 336 nm and 600 nm that correspond to $\pi - \pi^*$ transition of the phenyl ring and $n - \pi^*$ transition of benzenoid to quinoid respectively [29, 30]. In this work, we also obtained two broad bands close to those values especially at around 345 and 545 nm which may indicate characteristic absorptions of PANI. The absorption region of Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composite was between 200-600 nm for HP11, 200-650 nm for HP22 and 200-700 nm for HP33. More the amount of PANI increase, more the absorption region shows a slight redshift (bathochromic shift). This absorption is characterized by the passage of electrons from the valence band to the conduction band. The energy required for this transition is defined by the band gap energy $E_g$ given by the following relation [8, 31].

$$(ahv)^2 = B(hv - E_g)$$  

(4)

Where $A$ is a constant, $E_g$ is the band gap energy and $h$ is the Planck’s constant.
Figure 5. UV plots of Ba₀.₇Dy₀.₃Fe₁₁.₄Cr₀.₆O₁₉/PANI composite

Figure 6 shows Eg plots of prepared sample. The values of $E_g$ were determined by extrapolating the linear part of the graph of $(aHV)^2$ against $E_g$. Band gap energy values were found to be 1.96, 1.80 and 1.59 eV for HP11, HP22 and HP33 respectively. It can be observed that the value of band gap decrease with the increase in amount of PANI. This scenario was expected because due to the conductive nature of PANI the composite became more conductive with the increase in PANI amount and therefore the band gap value decrease. Similar observation has been reported by E. P. P. Athisayaraj and S. Chaturvedi [32, 33]. These obtained values are less than pure M-type barium hexagonal ferrite revealed by the literature (3.18 eV) [12].
5. Conclusion

Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$/PANI composites have been successfully synthesized using mechanical grinding after making Ba$_{0.7}$Dy$_{0.3}$Fe$_{11.4}$Cr$_{0.6}$O$_{19}$ and PANI by sol-gel method and oxidative polymerization method respectively. The formation of hexagonal ferrites was confirmed from XRD patterns and some traces of second phase (α-Fe$_2$O$_3$) were also observed. FTIR spectroscopy gave information about functional groups occurred from hexaferrite and PANI by the appearance of absorption peaks between 400-600 cm$^{-1}$ and 800-1600 cm$^{-1}$ respectively. The band gap decreases with the increase in PANI amount.

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