Synthesis, characterization and impedance studies of novel nanocomposites of gadolinium titanate

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Abstract: We report here a facile synthesis of Gadolinium doped titanate (GDT) nanocomposites (NCs) and their impedance, total current gain in the various concentrations of doped and undoped gadolinium to the titanate nanomatrix was investigated.GdTiO₃ NCs synthesized by co precipitation method using CTAB (cetyl trimethyl ammonium bromide) as capping agent triethyl amine under acidic condition at high temperature. Gd was doped (10-40 % molar wt) ratio, characterized by SEM (scanning electron microscopy), XRD (X-ray diffraction spectroscopy), UV Visible, CV (cyclic voltammetry) spectroscopic analysis. SEM crystal morphology indicated Gd x (TiO₃) 1-x was tetragonal close packing with the distribution of overlay of Gd is 50 nm, CV characterization revealed the oxidation potential of GdTiO₃ was + 0.34 eV. The aligned GdTiO₃ showed linear increase in the resistance with the different thickness of the pellet made from powdered NCs. Significant increase in the conductivity is due to varied thickness, decrease in the particle size, distinct grain boundaries. The modulus of the complex impedance (Z* ω) with respect to different current and voltage gain were measured by different size of the pelletized nanomaterials (~15 mm diameter, ~1-5 mm thickness, pressure of ~ 0.4 GPa) and the phase angle θ measured with different frequency range from 40 Hz to 2 MHz. The variation in the impedance (real and imaginary) depends on the grain boundary and grain size contribution at lower and higher frequencies. The conductivity due to grain (σg), grain boundary (σgb), calculated from the values of Rg andRgb (resistance at grain and grain boundary) and the specific grain boundary (σsgb) was calculated for the nanocomposites.

1. INTRODUCTION

The nanocomposites of rare earth metals finds applications as functional materials in building the hybrid compositional structures [1-3]. The various applications of these materials especially in the field of material science being one of the most remarkable achievements. The relative interactions occurring between the research in the electrical and electronic property studies required to overcome the existing challenges. The methods of synthesis, their characterization and the electronic properties, concepts and experimental procedures are well established to develop various types of materials such as electrochemical sensors [4], LEDs [5], biomedical devices [6], newer electrode materials [7-8], ultra-sensitive probes [9-10] to detect the various infections namely HIV, cancer. Novel directions in the field of electrical and electronic properties of these nanomaterials having hybrid composition...
especially in the current-voltage characteristics [11-13], impedance and photochemical properties (PCP). The deep insight studies of the nano compositional materials made of different rare earth metals highlighted the applications in the field of device fabrications and the structural materials were used to substantiate the enhanced IV characteristics, impedance of the materials, sensor characteristics etc. In recent years, enormous interest has been derived in establishing the novel hybrid nanocomposite materials made off rare earth. Recently, experimental reports on the carbon nanomaterials, fullerenes, the rare earth materials have not developed widely with respect to the diversified its applications in the field of electronics [14-18]. However, the isolated materials show the different results at different temperatures and the morphology of the hybrid materials determines the anatomy of their behaviour [19-21]. Another major feedback of these materials is particle agglomerations inside the cavity of the hybrid composition which makes the material relatively less stable in the fabricated structures. The objectives of this manuscript are to study the various electrical and electronic properties of the gadolinium titanate nanocomposites especially current, voltage, impedance, power dissipation, leakage current of the different thickness of the pelletized samples [22-24]. The synthesis of GdTiO₃ was carried out by co precipitation technique and the materials were subsequently purified by washing with ethanol and water mixtures several times, dried calcinated and made in the form of fine powders. The pelletized samples were subjected for the impedance studies at room temperature. The linear relationship of the impedance values [25-26] indicates the stability of the material, its response in terms of voltage gain and current gain in the semiconducting surface, less leakage current, more power dissipation factor of the titanate matrix doped with gadolinium. The present studies gives a pathway for the introduction of the rare earth metals which can be better donor or acceptor to elucidate for the better energy harvesting devices.

2. EXPERIMENT SECTION

2.1. Materials and Methods

The material required for the synthesis are procured from sigma aldrich, spectrochem, sd-fine chemicals and used without purifications. The deposition of the top contact is done using RF sputtering instrument procured from advanced process technology, material used is SS304, SS304L, and SS316. Base pressure is 10-7 torr and the substrate heating is available for 800 °C with electro polished process chamber and cryo pump. The solid supported SEM-EDS Zeiss Ultra 55 instrument with integrated energy and angle back scattered electron detector (EsB) and couple with Gemini high current mode has been used to closely understand the fusing of the material structures of p and n type. Powdered XRD (X-Ray Diffraction Spectrophotometer) Instrument from Rigka Smart Lab with Bragg- Brentano (BB) and Parallel Beam (PB) optics, photon max high flux 9kW rotating anode X-ray source coupled with a Hypix-3000 high energy resolution 2D multidimensional semiconductor detector having scintillation counter (SC), speed 1D (line) detector (D tex). Cu-Kα radiation (λ = 0.1542 nm) operating at 50 kV and 40 mA. UV Visible absorption spectrum was recorded using specord 210 plus analytic Jena equipped with variable spectral resolution and cooled double detection. The CV Characterization was performed by using CHI company USA (Austin) electrochemical analyzer model D630. Three electrode systems connected to the analyzer, Ag/AgCl as reference and Pt-wire as counter electrode. Current-voltage and impedance experiments were carried out by using Agilent B 1500 A series instrument (Keysight) with pulsed source of 5MHz measurements from 1 KHz to 5 MHz, 10ns pulsed IV resolution to understand the resistivity and capacitive properties of the nanocomposites. The sensor characteristic has been done using PVA fabricated microchip.

2.2. Synthesis of Gadolinium Titanate Nanocomposites GdTiO₃

The precursor for the synthesis of Gd-TiO₃ was Gd(NO₃)₃· 6H₂O (10-40 % molar wt. ratio) and TiCl₄ (titanium tetrachloride) were dissolved in deionized water under high acidic condition in presence of CTAB (cetyl trimethyl ammonium bromide) and triethanol amine as surfactant and capping agent in order to precipitate the titanate ions in gadolinium matrix. The reactants are brought to 85°C and continued stirring for 30 minutes. The precipitate obtained after cooling the reaction mixture was
ultra-sonicated for 2h at room temperature. The precipitate was filtered, washed with cold water and dried at 100-200°C. The dried solid was washed with ethanol, acetone to remove unwanted impurities, calcinated at 800-850°C to ground as fine nano-powders of gadolinium titanate.

3. RESULT AND DISCUSSION

3.1. Cyclic Voltammetry
The oxidation and reduction potentials were recorded by using cyclic voltamogram ‘figure 1’. Oxidation potential for the highest doped 40% was found to be – 0.47 eV and the reduction potential found to be + 0.13eV. The HTL (Hole Transport Layer) acting cathode material is titanate and the acting anode material is GT (donor), due to the increased donating ability of the Gd material, which intern increased electron donating ability leading to the more negative potential is observed in the heavily doped inorganic nanocomposites.

![Figure 1](image)

**Figure 1.** Typical illustration of the 40 % Gd doped titanate NCs CV spectrum

3.2. X-ray powder diffraction (XRD)
XRD patterns of the doped and undoped NCs recorded by powder X-ray diffractometer with CuKα(λ = 0.154 nm) ‘Figure 2’ show the XRD pattern of the inorganic nanoparticles of Gd-TiO$_3$ calcinated at 800 °C. XRD pattern of tetrahedral geometry of the intense peak TiO$_3$ was well matched with the JCPDS file. The particle size was calculated by sheeres equation of the intense peak and found to be 55 nm. The d-spacing of the undoped and doped NCs with respect to planes are the particle size of the doped and undoped nanoparticles calculated by Debye-sheers formula

\[ D = \frac{K \lambda}{\beta \cos \theta} \ A\]°

Where, D is average crystallite size, K is the shape factor, λ is the wavelength of X-ray, θ- diffraction angle and is the full width of the diffraction angle. The grain size of the Gd was higher than the grain size of the Gd-TiO$_3$ indicates that Gd doping is very essential to enhance the crystal growth of NCs.

![Figure 2](image)

**Figure 2.** XRD pattern of the 40 % Gd doped NCs
3.3. Scanning Electron Microscope

Morphologies of the doped and undoped nanoparticles were observed by SEM as shown in the ‘figure 3(a) and 3(b)’. The anomaly of the crystal structure was observed with decrease in the size of the nanoparticle of the undoped one than the Gd doped NCs. The rough surface morphology is responsible for increase in the surface area of the Gd doped NCs with observed particle size of 55 nm.

![Figure 3](image)

**Figure 3.** (a) Scanning electron microscopic images of the 40 % Gd-TiO$_3$; (b) SEM images of the undoped titanate

3.4. UV-Visible Characterization

The doped and undoped NCs were calcinated at 800 °C and the 40 % doped Gd NCs recorded for absorption using UV-Visible spectrophotometer ‘figure 4’. The solution was prepared using methanol solvent and placed in special quartz cells irradiated with UV radiation ranging from 100-800 nm. ‘Figure 4’ shows the absorption spectra of the 40 % Gd doped NCs with absorption ranging broadly from 450 nm to 700 nm (visible range) of the calcinated samples at 800 °C. ‘figure 4’ clearly shows the addition of Gd to the titanate leads to the displace the edge of UV-spectrum observed at 300nm, 325nm and increase in the absorptivity from 650 nm due to effect of addition of Gd into the titanate nanomatrix. The band gap energy of the samples recorded and calculated by kubeka mulk model and the direct allowed transition calculated using the formula

\[
(\alpha \ h\gamma)^2 = C (h\gamma - E_g)
\]

C-is the absorption coefficient, $h\gamma$-photon energy and $E_g$-optical band gap

![Figure 4](image)

**Figure 4.** UV-Visible spectrum of the 40 % Gd doped NCs with $\lambda_{max}$ at525 nm

4. IMPEDANCE MEASUREMENT

Inorganic rare earth metals like Y and Gd have drawn great interest from both academics and industry. Authors envisaged by the addition of rare earth metals like Gd to the titanate matrix can considerably change the NCs properties and emerge as new material. Co-precipitation method was adopted to precipitate the NCs of 40 % doped Gd-TiO$_3$ and was characterized by CV, SEM, XRD and UV-Visible spectroscopic techniques. Oxidative and reductive potentials, band gap, band energy were obtained from the CV experimentation which shows the 1.08 eV of band gap. The particle size, grain...
boundary distance and the shape of the NCs determined from the SEM, XRD measurements and the absorptivity and intern optical properties were attributed from UV-Visible spectroscopy. I-V characteristics (impedance, admittance) of the pelletized samples ‘figure 5, 6 & 7’ of 40 % Gd-TiO$_3$ in ‘figure 5’ showed non linearity in the total current gain and the calculated values of Impedance, conductance and the power dissipation factor depicted in table 1 & table 2. Values related to the I-V varies linearly, conductivity value varies from 3.25×10$^{-5}$ S to 4.75×10$^{-5}$ S. Impedance of the sample vary from 2.16 × 10$^{-4}$ to 2.62 × 10$^{5}$Ω. At 0.4 V and 1V the admittance value ‘figure 6 & 7’ was found to be 4.85 × 10$^{-5}$ to 4.23 × 10$^{-5}$ respectively. The values of Rgb varies from 77.00 Ω/cm to 1332.00 K Ω/cm with the increase in the applied voltage more and more negative value of the power dissipation was observed with the applied voltage. This research work opens up an idea and strategy to synthesize the rare earth doped NCs for the better performance of the photodiodes, sensors, light harvesting devices, LEDS and the construction of inorganic solar cells.

![Impedance of GDT (a)](image1)

**Figure 5.** Illustration of the impedance (I-V) curve of 20 % Gd doped NCs

![Impedance of GDT (b)](image2)

**Figure 6.** Representing the impedance (I-V) curve of 40 % Gd doped NCs
Figure 7. Representing the impedance (I-V) curve of 20%, 30% and 40% Gd-TiO$_3$

Table 1. A Representing the variation of conductance, impedance and admittance of the 40% doped samples.

| Samples$^a$ | Voltage [V] | Conductance [Siemens] $\times 10^{-5}$ | Impedance [Ohm] $\times 10^4$ | Admittance [Siemens] $\times 10^{-5}$ |
|------------|-------------|--------------------------------------|-------------------------------|-------------------------------------|
| Gd-TiO$_3$ | 0.2         | 3.25                                 | 2.62                          | 3.77                                |
| Gd-TiO$_3$ | 0.4         | 4.75                                 | 2.16                          | 4.85                                |
| Gd-TiO$_3$ | 0.6         | 4.52                                 | 2.26                          | 4.62                                |
| Gd-TiO$_3$ | 0.8         | 4.37                                 | 2.34                          | 4.57                                |
| Gd-TiO$_3$ | 1.0         | 4.23                                 | 2.52                          | 4.23                                |

$^a$(Samples of Gd-TiO$_3$ under different trails of IV)

Table 2. A Representing the variation of conductance, impedance and admittance of the 40% doped samples.

| Sample (GdTiO$_3$) | W g($1\times10^4$ radius/s) | Cgb (PF) | Temperature | R gb (K ohm) $\times g(10^6/cm)$ | $\mu$ ($10^6$/cm) |
|---------------------|------------------------------|----------|-------------|----------------------------------|-------------------|
| S1                  | 1.43                         | 0.09     | 300 K       | 13332.00                         | 0.09              |
| S2                  | 3.34                         | 2.45     | 300 K       | 975.00                           | 1.97              |
| S3                  | 3.25                         | 4.56     | 300 K       | 650.00                           | 2.57              |
| S4                  | 0.97                         | 0.08     | 300 K       | 077.00                           | 0.97              |
| S5                  | 2.25                         | 2.10     | 300 K       | 188.00                           | 5.57              |

5. CONCLUSION

Perovskite NCs materials were synthesized by co precipitation method using suitable reducing agent to control the size of the particles. The 40% Gd doped material was characterized by CV, grain and grain boundary distances were calculated from SEM and the shape of the amorphous NCs are elucidated with XRD. The pelletized samples were tested for their current-voltage characteristics indicates the non linearity in the crystal structure of the Gd-TiO$_3$ material and the increase and
decrease in the total current gain, capacitance, admittance and power dissipation factor is due to low electron density in the active layer Gd and the high surface conductivity. The device shows completely nonlinear I-V graphs at an optimal doping of 40% of gadolinium to the titanate matrix. Rgb values of the pelletized samples vary in between 188 K/ohm to 13332 K/ohm and Cgb values vary in between 0.08 to 2.45 (table 2). The obtained results could be applicable for the construction of novel hybrid materials for solar cells.

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