Effect of codoping of Rare Earth ions on Microstructure and Band Gap of Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm/Eu/Tb) Nanostructures Synthesized by modified hydrothermal method

Swaleha Naseem$^{1,3}$, Wasi Khan$^2$, Shakeel Khan$^1$, Shahid Husain$^3$

$^1$Department of Applied Physics, Z.H. College of Engineering & Technology, Aligarh Muslim University, Aligarh-202002, India
$^2$Department of Physics, Aligarh Muslim University, Aligarh 202002, India.

Abstract. Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$ and Gd$^{3+}$ ions have been incorporated in anatase TiO$_2$ nanostructures by a hydrothermally modified sol gel method. XRD data analysis revealed the formation of pure anatase phase that crystallizes in the tetragonal crystal symmetry without any secondary phase. FTIR spectra indicate stretching vibrations of bonds in the nanostructures. The absorption peak centered at 568 cm$^{-1}$ is related to the Ti-O-Ti stretching vibrations. Morphological studies and grain size estimation were performed by SEM measurements. SEM images depict nonuniform distribution of grains with a considerable variation in grain size. EDS measurements ensure chemical compositions in the samples. UV-visible absorption spectroscopy was used to study the optical properties. The doping of rare earth ions (Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) leads to the variation in band gap of TiO$_2$. Photoluminescence (PL) spectra indicate a significant change in the intensity on the doping of rare earth ions.

Keyword: TiO$_2$ nanostructures, XRD, SEM, Optical properties, fluorescence.

1. Introduction

Titanium dioxide (TiO$_2$) has polymorphic crystal structure namely; anatase, brookite and rutile, wherein anatase and brookite are metastable phases that convert to thermally stable rutile phase on heat treatment of 600 to 1200 $^\circ$C. Among these, anatase phase shows greater photocatalytic activity in comparison to other phases due to the formation of high hydroxylated surface in this phase that is responsible for photocatalytic reaction [1,2]. Hence, anatase phase becomes the subject of great interest. Anatase TiO$_2$ is a large bandgap (~ 3.2 eV) semiconductor with high refractive index (~2.52) and these properties has made rare earth ions to be doped in host TiO$_2$ lattice for having its applications in light emitting diodes, nano-integrated photonic devices, electronic displays, waveguides and highly reflective coatings [3-6]. In order to reduce the band gap of TiO$_2$, rare earth codoped system (La,N), (La,Fe) and (La,Y) were studied and predicted that La reduces the charge carrier recombination rates while N, Fe, Y reduces the band gap hence rare earth doped TiO$_2$...
nanoparticles can be used as efficient photocatalytic material[2,7]. On the other hand, lanthanides are rich in spectroscopic properties showing sharp emission spectra and photo-stability due to the parity forbidden intra f/f optical transitions with TiO2 that acts as a sensitizer[8]. In this, excited energy is transferred from the conduction band to the lanthanides f state and electron undergoes f/f transition that shows intense emissions. However, codoping of second rare earth ion bridges a bond among the host and first dopant that initiate energy transfer action [9,10]. It is known that the rare earth ions like Sm3+, Eu3+, Tb3+ and Gd3+ can enhance photocatalytic activity and luminescence properties that could be utilized for the opto-electronic devices and fluorescent markers in medicines being non-toxic and biocompatible in nature[11,12]. In this context, we have synthesized and investigated the microstructural and optical properties of rare earth ions codoped TiO2 samples.

2. Synthesis and characterization techniques
Titanium IV isopropoxide solution (C12H28O4·Ti), samarium oxide (Sm2O3), europium oxide (Eu2O3), terbium oxide (Tb2O3), gadolinium nitrate Gd(NO3)3·6H2O and absolute ethanol of AR grade were used as starting materials. Stoichiometric amounts of Sm2O3, Eu2O3, Gd(NO3)3·6H2O and Tb2O3 were dissolved in deionized water with the addition of nitric acid to obtain solution 1. Absolute ethanol is added to the titanium isopropoxide to make a solution 2, then solution 1 is added to solution 2 drop by drop and kept on stirring for 2 hours. The prepared solutions were hydrothermally treated at 160 ºC for 24 hours then obtained material was washed from deionized water. After washing samples were dried in an oven at 80ºC and ground to obtain codoped TiO2 samples in powder form. All synthesized samples of rare earth codoped TiO2 (A: Sm3+, Eu3+, Tb3+) were characterized through various analytical tools like x-ray diffractometer (XRD), scanning electron microscope (SEM) equipped with EDS, fourier transform infrared spectroscopy (FTIR), UV-visible and fluorescence spectroscopy. The phase purity of the samples was studied using Shimadzu XRD having CuKα radiation of wavelength (λ) = 1.5418 Å in the 2θ ranges of 20º to 80º. The FTIR spectra were registered at room temperature over the wavenumber range of 400-4000 cm⁻¹. Morphology and elemental analyses were observed by SEM (JEOL) equipped with EDS. UV-visible absorption and fluorescence measurements of the samples were performed using Perkin Elmer Spectrophotometer.

3. Results and Discussion

3.1. X-ray Diffraction
X-ray diffraction (XRD) profiles of rare earth codoped TiO2 samples were presented in Fig.1(a). The diffraction patterns of all the samples correspond to the tetragonal anatase structure without any other secondary phases of TiO2. The crystallite size (τ) was determined by employing the Scherrer’s equation, \( \tau = \frac{0.9\lambda}{\beta\cos\theta} \) (here λ stands for the wavelength of the x-rays and β is the full width at half maximum) from the most intense (101) diffraction peak. The average crystallite size was found to be 15.3, 9.6 and 6.4 nm for 1%@Sm3+-Gd3+, 1%@Eu3+-Gd3+ and 1%@Tb3+-Gd3+ codoped TiO2 samples. The reduction in the peak intensity and crystallinity may be due to the decrease in crystallite size and increase in the oxygen defects at the grain boundaries. The substitution of trivalent rare earth ions i.e. Sm3+-Gd3+, Eu3+-Gd3+ and Tb3+-Gd3+ on TiO2 lattice sites having larger ionic radii than Ti ion leads to distortion of TiO6 octahedra and creates oxygen vacancy for maintaining charge neutrality and also hinders the growth of TiO2[8,13]. The dopant ions produce a charge imbalance in TiO2 structure that induces the lattice disorder and hence due to which widening of peaks is observed.
3.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) samples are presented in Fig. 1(b). A broad absorption peak at 3378 cm$^{-1}$ is due to the hydroxyl group. This band corresponds to the Ti-OH on the surface and a sharp peak at 1620 cm$^{-1}$ is ascribed to the H-OH bending of the absorbed water. However, peak observed at 1032 cm$^{-1}$ in 1%Sm$^{3+}$-Gd$^{3+}$ codoped sample attributed to the C-O bending vibration that may be due to atmospheric carbon which diminishes in other codoped samples. The hump at 568 cm$^{-1}$ in all samples is ascribed to the Ti-O-Ti stretching vibration in TiO$_2$ lattice.

3.3. Scanning electron microscopy (SEM) and EDS

The morphological and microstructural analyses were performed by SEM measurements and shown in Fig. 2(a-c) for Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$). SEM micrographs revealed the occurrence of large collections of different non-uniform shape of the grains. It is seen that the surface morphology is highly affected by the doping ions. In order to identify the chemical elements in the prepared samples, energy dispersive x-ray spectroscopy (EDS) analysis was performed and shown in the inset of Fig. 2(a-c). EDS patterns ensure the presence of Ti, Sm, Eu, Tb, Gd and O elements that further confirm purity and good stoichiometric ratios in the doped samples.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** a) XRD profiles, and b) FTIR spectra of Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) nanostructures.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** SEM micrographs of a) Ti$_{0.98}$Sm$_{0.01}$Gd$_{0.01}$O$_2$, b) Ti$_{0.98}$Eu$_{0.01}$Gd$_{0.01}$O$_2$, and c) Ti$_{0.98}$Tb$_{0.01}$Gd$_{0.01}$O$_2$ nanostructures. Insets show the corresponding EDS spectra.
3.4. **UV-visible Spectroscopy**

Fig. 3(a) depicts the UV-visible absorption spectra of Ti$_{0.98}$Al$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) samples in the wavelength range of 200-600 nm. It is clear from the figure that the absorption edge is around 335-350 nm. The variation in absorbance depends on various factors like particle size, surface roughness, oxygen deficiency and impurity centers. Absorption peaks shift towards the higher wavelength i.e. red shift is observed with the codoping of Tb, Eu and Sm in TiO$_2$ lattice which may be attributed due to exchange interactions between localized electrons. The direct type band gap is confirmed using Tauc’s relation [14] [15] for all samples i.e. graph of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) and extrapolating the linear region of the plots (Fig. 3(b)). The calculated value of the bandgap is found to be 3.74 eV for Sm-Gd, 4.04eV for Eu-Gd and 4.22 eV for Tb-Gd codoped samples respectively. It is clear that the measured values of band gap are higher than the undoped TiO$_2$ (3.2 eV) sample.

![Absorbance spectra and Tauc plots](image)

**Figure 3.** a) Absorbance spectra, b) Tauc’s plots for Ti$_{0.98}$Al$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) samples.

3.5. **Fluorescence Spectroscopy**

Photo induced photoluminescence (PL) spectroscopy is a useful technique for the investigation of type and nature of the defects, energy levels and can afford information about the optical and structural properties of the material. In metal oxide nanoparticles, interstitial or vacancy of metal or oxygen ion creates point defects associated with the new energy levels created in the band gap region. The PL spectra of Ti$_{0.98}$Al$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) samples in the wavelength range of 200-600 nm was recorded at room temperature and shown in Fig. 4 with an excitation wavelength of 350 nm. It has been observed that the emission peaks of all the samples are almost identical but the intensity of the spectra decrease as reduction in the band gap of the samples from Tb to Sm ions. Recombination of electron and holes is directly related to the intensity of the photoluminescence spectra, however low intensity indicates a slow rate of electron and hole recombination indicating large number of charge carriers participating in the photochemical process. Thus, the fluorescence study suggests that the photonic behavior of the TiO$_2$ can be tuned by the incorporation of rare earth ions for extensive photonic applications [16].
Figure 4. PL spectra of Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A: Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) samples recorded at room temperature.

Table 1. Crystallite size, atomic% and optical band gap of Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A:Sm/Eu/Tb) samples.

| Sample      | Crystallite size $\tau$ (nm) | % atomic A/Ti | Energy band gap (eV) |
|-------------|------------------------------|----------------|---------------------|
| Ti$_{0.98}$Sm$_{0.01}$Gd$_{0.01}$O$_2$ | 15.3                        | 0.01           | 3.74                |
| Ti$_{0.98}$Eu$_{0.01}$Gd$_{0.01}$O$_2$ | 9.6                         | 0.008          | 4.04                |
| Ti$_{0.98}$Tb$_{0.01}$Gd$_{0.01}$O$_2$ | 6.4                         | 0.014          | 4.22                |

4. Conclusions
Codoped Ti$_{0.98}$A$_{0.01}$Gd$_{0.01}$O$_2$ (A:Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$) nanostructured samples were synthesized by hydrothermally modified sol gel method. Anatase phase of the samples was confirmed through XRD data analysis. The broadening of the peaks and average crystallite size confirm nanostructure form of the samples. FTIR absorption band centered at 530 cm$^{-1}$ attributes to the Ti-O-Ti bond that further indicates high purity of the samples. SEM micrographs support irregular and non-uniform distribution of the grains in all samples. EDS profiles ensure the presence of chemical elements in the doped samples. The optical bandgap was estimated by employing the Tauc’s relation and found to be 3.74, 4.04 and 4.22 eV for 1%@Sm$^{3+}$-Gd$^{3+}$, 1%@Eu$^{3+}$-Gd$^{3+}$ and 1%@Tb$^{3+}$-Gd$^{3+}$ codoped TiO$_2$ samples respectively. PL spectra exhibit significant change in the intensity of different codoped samples. Thus, the morphology and band gap of TiO$_2$ nanostructures can be finely tuned for the possible applications.

5. Acknowledgments
Swaleha Naseem is highly indebted to the University Grants Commission (UGC), India for providing Maulana Azad National Fellowship (MANF) (F117.1/201415/MANF-201415-MUS-UTT-33700/ (SAIII/Website)). Authors are obliged to the University Sophisticated Instrument Facility (USIF), AMU, Aligarh for providing microscopy facilities.
6. References

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