

ABSTRACT

In the last few decades, there has been a significant progress in the quest for suitable, efficient and affordable nanophosphors. In this regard, the rare-earth (RE) oxides and vanadate based nanosystems have drawn growing interest due to their excellent optical, optoelectronic properties and accordingly, their matchless scope can be realized in a wide and diverse range of applications. To name a few, are low threshold lasers, high performance luminescent panels, frequency up-converters, photocatalytic agents, drug-carriers, magnetic resonance imaging (MRI) contrast agent, bio-sensing and bio-labelling applications.

As an important host of rare earth oxide (REO), gadolinium oxide (Gd_2O_3) and gadolinium vanadate ($GdVO_4$) can accommodate suitable dopants especially transition metal or RE ions to yield nanophosphors of certain kind turning it to be extremely popular in processing efficient nanophosphors [1-6]. More precisely, the characteristic $5d-4f$ transitions can be influenced greatly with the incorporation of selectively chosen RE dopant and intentionally introduced defect states/trap centres via radiation exposure [7, 8]. Inclusion of lanthanide ions, such as Eu^{3+} with $5d \rightarrow 4f$, or $4f \rightarrow 4f$ transitions acting as emission centres [9], along with presence of trap centres such as lattice/intrinsic defects (e.g., oxygen vacancies, F-centres etc.) in the host matrix has proven to augment the bright and delayed emission responses [10, 11]. Use of co-dopants by incorporating non-RE dopant can also prove to be a vital tool in order to achieve enhanced luminescence, especially in case of nanophosphors [12]. $GdVO_4$ is of special interest from the optical window point of view since the excitation of the doping Ln cation through an energy transfer mechanism from the vanadate anion is much more efficient than the direct excitation of the Ln electronic levels.

This thesis highlights the investigations directed towards development of a multimodal luminescent material that has high phosphorescence efficiency as well biocompatible features. For this purpose, the host materials for Eu^{3+} activator ions have been evaluated for optimal luminescence with high emission intensity

profile for moderate doping and below quenching concentrations. To achieve asymmetry around activator ions, effect of defect creation due to γ -irradiation and inclusion of co-dopants in the host matrix has been evaluated. An approach has been made to understand the underlying mechanisms involved in the various processes involved.

'Chapter I' of the thesis includes discussion on introductory features highlighting essentially key features of RE oxide (Gd_2O_3) and vanadate ($GdVO_4$) systems. Beginning with the placement in the periodic table as a completely separated series called 'lanthanoids', the energy level diagram and phenomenon such as 'Shielding effect/Lanthanide contraction' and the related selection rules have been exemplified. The cytotoxic effects of the nanostructures keeping in mind their potential usage in biological applications as a theranostic agent has been detailed.

In *'Chapter II'* the synthesis protocol adopted for preparation of nanosystems including both bottom-up and top-down approach has been elucidated. Gd_2O_3 nanopowders doped with varying concentrations of Eu^{3+} were prepared by citrate gel route as well as hydrothermal route affirming cubic phase in the X-Ray Diffraction (XRD) analysis. Meanwhile solid state mixing- cum- sintering led Eu^{3+} doped orthovanadate ($GdVO_4$) nanosystem displayed zircon type tetragonal crystal structure. Transmission Electron Microscopy (TEM) imaging allowed us to visualize the nanocrystalline features of both undoped and doped nanosystems. The inter-planar distances measured from the lattice fringes using *ImageJ*[®] were found to be in good agreement with the XRD results.

The optical band gap of the as prepared nanosystem were determined from the optical absorbance spectra analysis following Kubelka Munk (KM) method. In the present case it was estimated as, ~ 5.5 eV for Gd^{3+} based oxides while was determined to be ~ 3.5 eV for the vanadate systems. The band gaps and phonon absorption energies for the systems, were also predicted through Kumar's model [13]. With the help of X-ray Photoelectron Spectroscopy (XPS) study, the valance band maximum was determined to be ~ 8.4 eV for oxide based nanosystems.

Inclusion of Eu^{3+} dopant into the vanadate matrix was also studied in detail and the VBM was found to be increased in this case. Upon Eu inclusion as dopant, peaks characteristic of +3 and +2 oxidation state of Eu, respectively. This important observation of the additional signal from +2 oxidation state of Eu, is attributed to 'surface valence transition' involved in the oxide system. Spin splitting can be witnessed from the $\text{Gd}4d$ spectra and contribution of spin polarization to the profile was found to be greater in the case of doped nanosystem.

With the aim and motive to probe and associate the electrically driven (ED) and magnetically driven (MD) transitions involved in Eu^{3+} , a thorough analysis of time resolved photoluminescence aspects was made employing time correlated single photon counting (TCSPC) capability (Horiba, USA) in 'Chapter III'. Concentration quenching was witnessed at a critical concentration of 3% $\text{Eu}^{3+}:\text{Gd}_2\text{O}_3$. Our analysis following Dexter's theory led to a stimulating observation wherein the quenching processes involved contributions from exchange interaction of ions. Furthermore, the average critical distance between the activator ions beyond which quenching can occur was determined using Blasse's energy transfer equation and was found to be $\sim 1.36 \text{ \AA}$ [14]. Following the emission profiles in the blue-green regime, it can be established that a large number of crystal field transitions influence these levels to follow non-radiative transitions between ${}^5D_1 \rightarrow {}^5D_0$. Out of the various transitions via ${}^5D_0 \rightarrow {}^7F_J$ ($J=0,1,2,3,4$) in the red and far red regime the ${}^5D_0 \rightarrow {}^7F_0$ transition, positioned at $\sim 580 \text{ nm}$ is a captivating observation confirming J-mixing due to crystal field perturbation and/or mixing of low lying charge transfer states into wavefunctions of $4f_6$ configuration. PL emission profiles of γ -irradiated samples further relates the effect of distorted local field leading to peak splitting. Point defect formations due to 1.3 MeV gamma irradiation induced creation of closely packed non-radiative trap centres offered both neutral as well as ionized vacancies. Hence, it would indicate two possible excitation pathways to populate the 5D_0 level, one being via 5D_1 level and the other promoting ions directly into 5D_0 state. Non-radiative relaxation caused by the surface defects acting as quenchers was

also observed after irradiation. Further study can be extended considering other RE oxides with Eu^{3+} inclusion.

In '*Chapter IV*', γ -irradiation induced manifested PL $\text{GdVO}_4:\text{Eu}^{3+}$ nanosystems and related phosphorescence decay dynamics' has been discussed in detail. From the excitation spectra, energy transfer from $[\text{VO}_4]^{3-}$ tetrahedral ions to Eu^{3+} was found to display predominant excitation route. Furthermore, luminescence concentration quenching beyond 3% $\text{Eu}^{3+}:\text{GdVO}_4$ was realised with critical quenching distance between activator ions in the matrix being $\sim 1.83 \text{ \AA}$ as determined from the Blasse's energy transfer equation. In addition, gamma irradiation induced luminescence quenching of Eu^{3+} emission profile was also evaluated. Furthermore, decay lifetime decrement with increasing irradiation dosage could be observed from the lifetime decay dynamics.

Raman characteristic of $\text{GdVO}_4:\text{Eu}^{3+}$ nanosystems are discussed in *Chapter V*. Various Raman active modes are observed in the Raman spectra of the samples. Important observations of ($\nu_2 \sim 380 \text{ cm}^{-1}$) symmetric V-O stretching or O-V-O bending mode, ν_2 mode $\sim 880 \text{ cm}^{-1}$ vibrational structure (stretching internal vibration in $[\text{VO}_4]^{3-}$ anionic group and ν_3 modes ($\sim 800\text{-}820 \text{ cm}^{-1}$) overlap of two E_g and B_{1g} modes have been discussed. Relaxation of E_g and B_g modes in ν_3 components upon Eu inclusion beyond critical concentration was determined and interestingly, partial *zircon* to *scheelite* type transition upon Eu^{3+} co-doping has been realized. Effect of structural disordering leading to the observations made upon Eu^{3+} inclusion has been expounded upon in this chapter.

A superior photocatalysis of azo based dyes has been speculated recognizing that the GdVO_4 nanosystem comes with an excellent capability to generate hydrogen from water [15, 16]. In '*Chapter VI*' the photocatalytic performance of the as-derived nanocatalysts against azo dye-CR has been highlighted considering daylight and UV illumination. The CR dye was apparently degraded to the tune of $\sim 91.8\%$ by 3% $\text{Eu}^{3+}:\text{GdVO}_4$ nanocatalyst, possibly to other aromatic species, with convincing discoloration effect. Notably, the rate constant gets doubled with the inclusion of dopant into the host. A better understanding of the photocatalytic

processes and the operative conditions could offer great opportunities for its industrial relevance.

A dependable approximation of erythrocyte deformability and processes involved are requisite for optimal evaluation of diagnostic features as well as therapeutic characteristics elucidated in *Chapter VII*. To be specific, hemocompatibility of 3% $\text{Eu}^{3+}:\text{GdVO}_4$ nanosystem was proven to be better than 3% $\text{Eu}^{3+}:\text{Gd}_2\text{O}_3$. In addition, dose dependent effect in plasma recalcification time has also been observed such that plasma coagulation time almost halved upon treatment with 100 $\mu\text{g}/\text{ml}$ vanadate based nanosystem. The cells fixed with glutaraldehyde after 1 h and 12 h of treatment with the nanosystems suffered damage and shape transformations as observed from Scanning Electron Microscopy imaging. The percentage of transforming/damaged cells increased upon incubation for 12 h such that the number of viable healthy cells was high for $\text{Eu}^{3+}:\text{GdVO}_4$ system.

'Chapter VIII' of the thesis draws conclusions from the investigations performed and observations made in the present study. The important findings are highlighted with their scope and their relevance in future studies are emphasized.

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