ABSTRACT

In recent years, nanoscale luminescent systems have gained remarkable research interest as their size and shape have tremendous influence on their physical, chemical, optical, optoelectronic and magnetic properties [1]. The anisotropic growth of one-dimensional (1D) systems under controlled environment, has led to the fields of growing interest which have immense potential in the areas of nanophotonics, nanoelectronics and other functional elements [2,3]. On the other hand, rare-earth (RE) based nanostructures are extremely promising in the field of high performance luminescent components, nanophosphors, catalysis and other functional devices due to their unique electronic, optical and physicochemical responses arising from *4f* electrons [4,5].

Gadolinium oxide (Gd_2O_3) is known for their excellent thermal and chemical stability apart from exhibiting narrow emission line [6]. It is a useful candidate in the deployment of waveguide devices, high dielectric constant components and similar devices [7]. On the other hand, elongated RE oxides have recently been applied to drug delivery and competitive immunoassays [8]. For practical purposes, gadolinium (III) chelates are in extensive use as magneto-resonance imaging (MRI) contrast agents. Recently, it is reported that depending on the particle diameter (d), gadolinium oxide nanoparticles are capable of exhibiting larger longitudinal relaxivity values than gadolinium (III) chelates. Therefore, the former have emerged as an excellent candidate to be used as MRI contrast agent [9].

This thesis highlights structural, optical and optoelectronic responses of nanometric Gd_2O_3 and $Gd_4O_3F_6$ systems both in pure and doped forms. Physico-chemical and hydrothermal routes have been employed for growing nanoparticles and nanorods under suitable environment. An optimal RE (Tb^{3+}, Eu^{3+}) doping is also emphasized to evaluate *D-F* transitions in Gd_2O_3 and $Gd_4O_3F_6$ nanosystems. Moreover, the effect of 80 MeV energetic carbon ion irradiation on Gd_2O_3 nanorods is investigated to exploit morphology, optoelectronic and spin-spin relaxation features. Physical and biophysical

characteristics of Gd_2O_3 nanoparticles and nanorods are also assessed. Furthermore, the magneto-rheological property of Gd_2O_3 nanorods is examined before and after 1.25 MeV γ-irradiation.

The *Chapter I* is an introductory chapter which highlights fundamental aspects of rare earth oxide and oxyfluoride systems. Several important features, like luminescence response, radiation effect, bio-physical characteristics and rheological properties are being discussed in the light of existing literature and recent reports. This chapter gives an overall account on the present status, challenges as well as the importance of materials to be investigated for certain specific applications.

In *Chapter II*, the synthesis and basic characterization of pure and doped Gd_2O_3 nanosystems are described. The visible evidence of different nanostructures like nanoparticles, nanorods along with their structural analyses have been presented. Oriented attachment (OA) mediated characteristic growth of Gd_2O_3 nanorods from the nanoparticle seeds is also discussed [10]. The crystallographic information was revealed by a Rigaku miniFlex X-ray diffractometer (XRD) that uses a CuK_α source (λ=1.543 Å). The diffraction angle was varied in the range of 20^o to 60^o and with a step angle of 0.05^0. Transmission electron microscopy (TEM) images were recorded by a JEOL JEM 2100 or a TECNAI G2 20 S-TWIN machine, operating at an accelerating voltage of 200 kV. The optical absorption study was performed by a UV-Visible spectrophotometer (UV 2450, Shimadzu). Raman measurements were recorded by using a Renishaw In-Via Raman spectrometer (Rensihaw, Wotton-under-Edge, UK) equipped with an Ar^+ laser of λ=514.5 nm used as the excitation source. The Raman spectra were acquired with a measured resolution of 0.3 cm^{-1}. The room temperature photoluminescence emission and electron paramagnetic resonance data have been acquired by using a PerkinElmer LS 55 spectrophotometer and a JEOL: JESFA200 EPR spectrometer; respectively. Lastly, magnetic hysteresis measurement was carried out at room temperature using SQUID (Evercool SQUID VSM DC magnetometer, Quantum design, USA).

The impact of 80-MeV C^{6+} ion irradiation on the morphological, interrelated emission response and spin- spin relaxation features of the Gd_2O_3 nanorods are presented in *Chapter III*. On increasing the irradiation fluence between 1×10^{11} and 3×10^{12} ions/cm^2, the emission associated with neutral oxygen vacancies (V_{Ox}), positioned at ~350 nm, underwent a steady increase compared to that associated with the singly charged vacancies (V_O^+), located at ~414 nm. The enhancement of spin–spin relaxation time (τ_{ss}) is ascribed to a substantial changeover (from V_O^+ to V_{Ox} defects) with irradiation, V_O^+ being recognized as the major contributor to paramagnetic centres [11].

The *Chapter IV* focuses on the optical properties of the pure and RE ion doped $Gd_4O_3F_6$ nanostructures analyzed through optical absorption and photoluminescence (PL) spectroscopy studies. In particular, the effect of RE doping on the *D-F* transition mediated optical emission in rare earth oxyfluoride system is discussed. Furthermore, intra *4f* transitions of Eu^{3+} ions are recognized in the host $Gd_4O_3F_6$. On the other hand, Judd-Ofelt (J-O) parameter of Eu^{3+} ions has been calculated from the emission spectra of Eu^{3+} doped gadolinium oxyfluorides samples [12].

The *Chapter V* gives a detailed description on the magneto-rheological behavior of the pristine and γ-irradiated gadolinium oxide based nanorod systems. The typical flow curve of our synthesized samples exhibited non-Newtonian characteristics. The rheological plots displayed a non-Newtonian power law ($\eta_v = K_v \dot{\gamma}^m$) behavior having power indices (m) varying in the range of 0.43–0.5. The apparent viscosity of the fluids increased with increasing the magnetic field.

Physical and biophysical landscapes of nanoscale Gd_2O_3 systems relevant to human red blood cells (RBCs) and cancer cells are presented in *Chapter VI*. The cell-cytotoxicity assays, hemolytic against human RBCs analysis demonstrate excellent biocompatibility of our Gd_2O_3 nanosystems. The prepared samples also inhibited the growth of HepG2 and MDA-MB231 cancer cells, but to different extent. Realizing a stronger impact by the latter cell type, the cell viability was observed to be significantly lowered, to an amount of ~65 and 57% on treatment with GNP and GNR systems (at 100 μg/mL); respectively. Moreover, the apoptotic analysis has been worked out for the aforesaid cell lines.

Lastly, in *Chapter VII*, the conclusions drawn from the present investigation are highlighted along with important findings and their relevance in future works.

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