PREPARATION AND CHARACTERIZATION OF SELECTED LUMINESCENT NANOPARTICLES

The luminescent nanoparticles have been an important and interesting research topic for many years. Luminescent nanomaterials come in many forms such as nanoparticles, nanoclusters, quantum dots, tubes, wires, cages, balls and nanostructured units. They compose of rare earth elements, semiconductors, metal oxides, inorganic and organic polymers. Research in luminescent nanoparticles provide challenges to both fundamental research and breakthrough development of technologies in various areas such as electronics, photonics, nanotechnology, display, lasing, detection, optical amplification, fluorescent sensing to biomedical engineering and environmental control. Strontium Barium Niobate (SBN) and rare earth doped SBN were selected as luminescent nanoparticles for the study. SBN is an attractive material being widely used in diverse applications.

Strontium barium niobate, $Sr_xBa_{1-x}Nb_2O_6$ ceramics abbreviated as SBN are ferroelectric materials with tungsten bronze structure, a P4bm space group exhibit excellent electro-optic, pyroelectric, nonlinear optical properties and photorefractive properties. The photorefractive properties of SBN system can be enhanced by suitable dopants. Good electro-optical and nonlinear optical properties make SBN a very interesting material for technological application like frequency doubling, optical parametric oscillation and optical storage of information. A number of trivalent rare earth dopants have been incorporated into the host SBN for different purposes and their spectroscopic properties have already been analysed. Usually SBN ceramics are prepared by the traditional solid-state reaction method which requires high sintering temperature and results in poor compositional homogeneity. Therefore, the thesis presents the preparation of nanosized SBN and rare earth doped SBN ceramic powder systems by sol-gel process. The structural characterization was done by (TG/DTA), Fourier Transform Infrared

Spectroscopy (FTIR), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), Raman Spectra and optical properties were studied by UV-Visible absorption spectroscopy, Photoluminescence (PL), Colorimetry, Judd–Ofelt (J-O) approach and Time-Correlated Single Photon Counting (TCSPC). Also the SBN ceramic systems are identified as potential optical limiters at 532 nm excitation wavelength. A comparison of structural and optical properties of SBN and rare earth (Eu^{3+}, Sm^{3+} and Nd^{3+}) doped SBN samples in bulk form were also investigated.

The thesis is divided into seven chapters and the chapter wise summary of the same is given below.

Chapter 1 begins with a general introduction on luminescent nanomaterials, a brief review of the reported work done on SBN and the application of such systems in various fields. The structure of SBN ceramic system, synthesis through sol gel and solid state reaction methods, the advantages and disadvantages of the methods are also briefly summarised. The spectroscopic properties of rare earth (Eu^{3+}, Nd^{3+} and Sm^{3+}) ions and different f-f transitions of these ions are outlined. The different structural characterization techniques used in the present work are discussed. The optical studies such as UV-Visible absorption spectroscopy, Photoluminescence, Colorimetry and Time Correlated Single Photon Counting (TCSPC) are briefly discussed.

Chapter 2 discusses the preparation of SBN, Eu^{3+}, Sm^{3+} and Nd^{3+} doped SBN nano and bulk ceramic systems using sol-gel and solid state reaction methods. The systems were characterized by XRD, FTIR, TG/DTA and Raman spectra. Particle morphology of the systems has been examined using SEM. The nano and bulk crystallite size were confirmed from HRTEM images. Incorporation of Eu^{3+}, Sm^{3+} and Nd^{3+} in the host was confirmed by the Energy Dispersive X-ray studies. The broad and strong Raman peaks at 260 and 625 cm^{-1} also suggests the tungsten bronze structure of SBN.

Chapter 3 details the optical properties of SBN, Europium [Eu^{3+}] ion doped SBN nano and bulk ceramic systems prepared using solid state and sol-gel methods. A broad

emission in the UV region extending to the visible was observed when excited at 305 nm for SBN nano and bulk systems. This emission is attributed to charge transfer vibronic exciton (CTVE). The absorption in the samples is from direct transition and the values of energy gap were calculated for SBN and SBN:Eu systems. With decreasing particle size, the excitonic transition is shifted towards higher energies. The fluorescent spectra of SBN:Eu nano ceramic system reveals that the characteristic emission of europium ion increases considerably than that of the bulk. The ratio of the integrated intensities of the hypersensitive $^5D_0 \rightarrow {}^7F_2$ and the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ is 5. This value indicates that Eu^{3+} is accommodated in non centrosymmetric sites. The luminescent decay of SBN and SBN:Eu nanosystems are multi exponential. The richness of the red color of SBN:Eu has been verified by determining their color coordinates from the CIE standard charts. The systems were analyzed and discussed aiming to be applied in photonic technology.

Chapter 4 presents the optical properties of Samarium [Sm^{3+}] doped Strontium Barium Niobate (SBN) nano and bulk ceramic systems. The absorption in the samples is from a direct transition and the values of energy gap were calculated for bulk and nano SBN:Sm systems. The excitation spectrum of nanosized Sm^{3+} doped SBN shows intense peaks at 406 and 478 nm. Orange-red emission was obtained for nano SBN:Sm, when excited at 406 nm. From the measured decay profiles, the tri- exponential lifetime of the systems were calculated. The color coordinates of the samples were calculated using colorimetric studies. The Samarium doped Strontium Barium Niobate ceramic systems can be used as orange-red phosphor in the solid state lighting devices.

Chapter 5 discusses the importance of Judd–Ofelt (J-O) approach and the optical properties of nano sized and bulk Neodymium [Nd^{3+}] doped SBN ceramic systems. The phenomenological intensity parameters were obtained using the Judd–Ofelt (J-O) approach. The J-O intensity parameters were used to calculate the spontaneous radiative transition probabilities, radiative lifetimes and branching ratios of the Nd^{3+} transitions from the upper multiplet manifolds to the corresponding lower-lying multiplet manifolds $^{2S+1}L_J$ of Nd^{3+}. The transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ in Nd^{3+} doped SBN ceramic system shows the highest branching ratio and integrated absorption cross-section. Therefore the transition

$^4F_{3/2} \rightarrow {^4I_{11/2}}$ in Nd^{3+} doped SBN ceramic systems could be a potential candidate for various photonic applications.

Chapter 6 discusses the nonlinear absorption behavior of pure SBN and rare earth (Eu^{3+} and Nd^{3+}) doped SBN nano ceramic systems which has been investigated employing the open aperture Z-scan technique using 532 nm, 5 ns laser pulses. The effective three-photon anano ceramic systems. The three-photon absorption coefficients of pure SBN, SBN:Eu and SBN:Nd bulk ceramic systems were also calculated as 1.2 $x10^{-23}$ m^3/W^2, 5.8 x 10^{-23} m^3/W^2 and 9.1 x 10^{-23} m^3/W^2 respectively. It is found that these materials are potential optical limiters at this excitation wavelength.

Chapter 7 describes the conclusion and future scope of works. This chapter sums up the salient features of the work described in this thesis and the scope for potential investigations in this field.

The research work presented in the thesis has either been published or communicated to reputed peer reviewed international journals, conference proceedings and presented in various national/international seminars

Papers published in International Journals

1. *Nonlinear Optical Properties of Nanosized Rare Earth Doped Strontium Barium Niobate Ceramics,* J. Nuja, Suchand Sandeep C.S, Reji Philip and Nandakumar K., Spectroscopy Letters 44 (2011) 334-339.
2. *Structural and Photoluminescence Studies on Nanosized Samarium- Doped Strontium Barium Niobate Ceramics,* J. Nuja and N. Kalarikkal, Spectroscopy Letters 45 (2012) 184-189.
3. *Structural and Luminescent Studies on Samarium doped Srontium Barium Niobate,* Nuja J. and Nandakumar K. (Communicated to Journal of Luminescence-2011).
4. *Red Luminescence of Eu^{3+} ions in SBN ceramic system,* Nuja J. and Nandakumar K. (Communicated to Journal of Rare Earths-2011).
5. *Fluorescence and Radiative Properties of Nd^{3+} Doped in SBN Ceramic System,* Nuja J. and Nandakumar K. (Communicated to Journal of Fluorescence-2012).