The development and renewed interest in solid state optical materials have led to the improved techniques for their synthesis and characterisation. Spectroscopic techniques are widely employed as important characterisation tools with special emphasis on their applications in electrochromic displays, chemical sensors, energy storage devices and solar energy converters, to name a few. In this context, phthalocyanine and porphyrin systems in solid matrices have attracted a great deal of attention recently because of their unique properties such as semiconductivity, photoconductivity and chemical activity. In particular, phthalocyanines have the advantage of being very stable against thermal and chemical decomposition and present very intense optical absorption in the visible. These properties favoured them to serve as active materials for molecular electronic devices. Further, more interest in phthalocyanine compounds has recently been renewed due to the discovery that they form metallated compounds. In a parallel direction a high level of interest has been devoted to exploiting porphyrin type systems with strong absorption in the VIS-NIR for various applications ranging from sensors and novel optical materials to the development of superior photosensitizers. It is also an inherent necessity for such systems that the photosensitizer absorbs strongly throughout the visible region and possesses a relatively long excited state lifetime. Such an enhanced lifetime is manifested by these systems embedded in solid matrices.

During the past decade, there has been an enormous growth in the interest in the sol-gel processing of glasses, ceramic materials and thin films. The motivation for the synthesis of sol-gel monoliths is primarily due to higher purity, homogeneity, lower processing temperatures and control over microstructure associated with sol-gel compared with traditional glass melting. The key to sol-gel lies with its versatility and relative ease of production, which leads to nonlinear materials, laser materials and optoelectronic devices depending upon the dopants incorporated into the host. The spectroscopic properties of these materials play an important role in their use in device applications. Therefore, the spectroscopic techniques for elucidating the structural and optical properties of the materials take the highest priority.

The thesis presents a detailed account of the spectroscopic analysis of phthalocyanine/porphyrin embedded in melt prepared borate glasses. The thesis
also provides detailed spectroscopic studies and structural evolution of transition metal/rare earth ion doped glass monoliths derived from sol-gel process.

Chapter 1 presents a general introduction on glassy materials and their methods of preparation. The physical processes are discussed in a more general way with special emphasis on glass formation from melt and sol-gel processing. The structure and topology of the glassy matrices are described in detail with various networking models. The advantages and merits of glasses as hosts for phthalocyanine, porphyrins, transition elements and various rare earth ion species are detailed. The spectroscopic and optical features of rare earth ions in glasses, which are instrumental in arriving at qualitative and quantitative results, are described. The importance of the Judd-Ofelt theoretical analysis of rare earth ions in condensed media is also touched up on.

Chapter 2 deals with the optical absorption and emission spectral measurements of various phthalocyanine (Pc) doped borate glassy matrices. Absorption measurements have been done corresponding to photon energies in the range 1.1 - 6.2 eV for H₂Pc, MnPc, FePc, NiPc, CoPc, CuPc, ZnPc and MoOPc systems. Several new discrete transitions are observed in the UV-VIS region of the spectra in addition to a strong continuum component of absorption in the IR region. Values of some of the important optical constants for the relevant electronic transitions are evaluated and all the data reported for Pc-s in the new matrix have been compared with those corresponding to solution, vapor and thin film media. All the emission spectra show intense fluorescence peaks in the 765 nm region upon excitation in the B-band (330 nm) and Q-band (700 nm). Fluorescence intensity is found to be minimum in the free base phthalocyanine (H₂Pc) whereas maximum in the MoOPc. Analysis of the emission data yielded spectral parameters favoring high optical amplification in the 765 nm region.

Chapter 3 describes the optical properties of free and substituted porphyrins (PP) doped borate glassy matrix. Absorption spectral measurements of H₂TPP, CdTPP, MgTPP and ZnTPP doped borate glassy matrix have been made in the 200-1100 nm region and the spectra obtained are analysed to obtain the optical band gap (Eₙ) and other important spectral parameters viz. oscillator strength (f), molar extinction coefficient (ε), electric dipole strength (q²), absorption cross-section (σₐ) and molecular concentration (N). Intense fluorescence was observed in the region 668-685 nm for CdTPP, ZnTPP and
MgTPP doped matrices, whereas no such fluorescence was observed in H$_2$TPP doped matrix. Fluorescence intensity was observed to be almost similar in all the metallated porphyrin matrices. Fluorescence bandwidth ($\Delta \lambda$), decay time ($\tau$), stimulated emission cross section ($\sigma$) and optical gain ($G$) of the principal fluorescence transitions corresponding to the Q-band excitation were also evaluated and discussed.

**Chapter 4** discusses the synthesis and spectroscopic characterization of silica gel monoliths containing trivalent chromium. The gels doped with Cr$^{3+}$ are prepared by selected process parameters, such as sol pH, water-alkoxide ratio, aging, drying and heat-treatment. By an accurate control of these parameters high optical quality homogeneous silica glass samples containing chromium were prepared. The UV-VIS absorption spectra, FTIR spectra, and fluorescence emission spectra of the silica glass samples and their in-process gel were recorded and analyzed. The UV visible spectra of the gels dried at 60°C indicated only the presence of Cr$^{3+}$ ions and no Cr$^{6+}$ (~345nm) ion was observed. Electron spin resonance studies showed that concentration of Cr$^{5+}$ increased with increasing heat treatment temperatures. On further heat treatment the conversion of oxidation states (Cr$^{3+} \rightarrow$ Cr$^{6+}$) occur and the existence of these states was confirmed through spectral measurements. The FTIR spectra showed that high temperature heat treatment could greatly reduce the amount of OH groups and organic residues in the silica. It was also observed that a high OH content contributes to the fluorescence inefficiency of the gels as well as porous glass.

**Chapter 5** is concerned with the preparation of the silica matrices doped with Dy$^{3+}$ rare earth ion by sol-gel technique and the study of spectroscopic properties in dried gels and gel glasses. From the optical absorption data, Judd-Ofelt ($\Omega_2$, $\Omega_4$, $\Omega_6$) parameters are derived. The calculated values of the J-O parameters are utilized in evaluating the various radiative parameters such as electric dipole line strengths ($S_{ed}$), radiative transition probabilities ($A_{RAD}$), radiative lifetimes ($\tau_{RAD}$), fluorescence branching ratios ($\beta_R$) and the integrated absorption cross sections ($\sigma_\alpha$) for stimulated emission from various excited states of the rare earth ion. The structural changes during the gel to glass transition of the silica xerogels were studied using the fluorescence properties of the Dy$^{3+}$ ion. The fluorescence intensity ratio (yellow to blue ($Y/B$)) is used as a measure of the symmetry of rare earth ion environment during the gel - glass conversion. The high value of the intensity
ratio of the 1000°C heated gel showed that the rare earth ions are embedded in the glassy silica network with an asymmetric environment. Fluorescence data are used to understand the effect of metal cation codopants on the state of aggregation of rare earth ions in sol-gel silica. The addition of codopants inhibits the clustering of rare earth ions and promotes better dispersion with the generation of strong crystal field bonding sites for rare earth ions.

The work presented in the thesis has been published/communicated in refereed international journals, conference proceedings and presented in various seminars/symposia.

**Research papers published/communicated**


**Papers published/communicated on topics not included in the thesis**

7 Studies on the growth and optical characterization of dysprosium gadolinium oxalate single crystals Cryst. Res. Tech (communicated)
8 Photovoltaic characterisation of luminescent anti reflection coatings of Sm$^{3+}$ in silica matrix. Thin Solid films (communicated)
9 Phonon sidebands and local vibrational analysis of Eu$^{3+}$ doped silica glasses J. Sol Gel Sci. Tech. (communicated)
10 Application of standard and modified Judd-Oftelt theory to Pr$^{3+}$ doped phosphate and sol-gel silica glasses Phys. Chem. Glasses (communicated)

Research papers presented/accepted for presentation in symposium
1 Judd-Oftelt Analysis of Nd$^{3+}$ in borate glasses. DAE-BRNS symposium on Spectroscopy of Lanthanides and Actinides, BARC, Mumbai (1999)
4 Upconversion fluorescence in ZnONa$_2$PO$_4$: Sm$^{3+}$ glassy matrix, Proceedings of the international conference on laser materials and devices, DSC, New Delhi, Allied Pub. Ltd. (2000)
5 Spectroscopic investigations of Cr$^{3+}$ doped silica gels. Current trends in materials science, Mahatma Gandhi University Kottayam (2001)