CHAPTER 1 INTRODUCTION

1.1 Background

Nowadays, there has been an increasing interest in the synthesis and characterization of structure and physical properties of heavy metal oxide (HMO) glasses due to their high refractive index, high density, high nonlinear optical susceptibility, high infrared transparency and good radiation shielding for γ - rays. Heavy metal oxide based glasses such as bismuth oxide based glasses have attracted the scientific community due to its important applications of thermal and mechanical sensors, reflecting windows, glass ceramics etc. [1-4]. Bi_2O_3 possess high refractive index, and exhibit high optical basicity, large polarizibilty and large optical susceptibility values [5-7] which make them ideal candidates for applications as infrared transmission components, ultra fast optical switches, and photonic devices. Moreover, the HMO such as lead or bismuth oxide containing glasses shows extremely high radioactive resistance because of their high density and atomic number. Currently lead oxide glasses have been restricted in various applications as it is hazardous to health and environment [8]. In this context, bismuth oxide has been a suitable substitution of lead oxide in glass preparation for its high refractive index, non-toxicity, bismuth oxide alone cannot be considered as network former due to small field strength ($z/a^2 = 0.53$, where z = formal valency and a = internuclear distance) of Bi^{3+} ion [9]. However, in combination with other glass formers, the glass formation is possible in a relatively larger composition range [10]. Due to their ideal combination of high γ-ray absorption coefficient (imparted by their large atomic mass) and good glass forming ability as oxides, Bi is useful in γ - ray absorbing windows in the nuclear industry and high energy physics [11-17]. Requirements for these glasses are in general similar to that for nonlinear optics, HMO glass is needed for a good attenuation factor, but moderate concentrations of traditional network formers are allowed, facilitating fabrication of the thick parts needed for good shielding [18].

Boric acid (B_2O_3) is one of the most popular and excellent glass formers known and can form glass alone at lower melting point with good transparency, high chemical durability, thermal stability and good rare earth ion solubility [19]. Because of its higher bond strength, lower cation size and smaller heat of fusion, so the structural investigation of boron in these glasses is one of the most attractive points of borate glass formation and related doped systems. In borate glasses, B^{3+} ions are triangularly coordinated by oxygen atoms and the triangle units are corner bounded in a random configuration. It was reported that addition of a network modifier in borate glasses could produce the conversion of the triangular BO_3 structural units to BO_4 tetrahedral with a coordination number four [20]. Normally, glass with B_2O_3 alone possesses high phonon energies (~ 1300 cm^{-1}) and cannot suppress nonradiative decay process and hence rare earth ion emissions are strongly reduced. Borate glasses have many advantages as a material for radiation dosimeter applications in view of the fact that their effective atomic number is very close to that of human tissue as well as it relatively low electrical conductivity [21].

Zinc oxide (ZnO) is one of the important constituent components in the formation of oxide glasses and in particular, it is known that glasses containing large amounts of ZnO have low melting temperatures. Because low melting glasses with large amounts of PbO, which have been used widely in various commercial devices, are now unfavorable from the environment point of view, the importance of low melting glasses with large amounts of ZnO and with no PbO is increasing largely. Indeed for instance, ZnO - B_2O_3 glasses with high ZnO contents have been used as a sintering aid for the fabrication of low temperature eco - fired ceramics. Glasses with high ZnO contents, therefore, are very attractive materials [22]. From above reviews, the zinc bismuth borate (ZBB) glasses are preferred as they possess low melting temperature (easy to synthesis at normal condition in laboratory), large refractive index, good physical and chemical properties (large glass forming region, high thermal stability, good rare earth ions solubility and a large window transmission) [23].Zinc oxide based glasses have special applications in the area of varistors, dielectric layers and transparent dielectric and barrier ribs in plasma display panels [24, 25].

Over the last several years, glasses doped with rare earth (RE) ions are proving to be luminescent materials as they have high emission efficiencies. These emissions correspond to 4f - 4f and 4f - 5d electronic transitions in the rare earth ions. The 4f - 4f transition gives an especially sharp fluorescence pattern from the ultraviolet (UV) to the infrared (IR) region [26]. Among all the rare earth ions, europium (Eu) ion have attracted significant attention, because they have a large potential for applications in some optical fields, such as lasers, fiber amplifiers, phosphors, electroluminescent devices and high density optical storage [27-36]. We have undertaken the present work to analyze the influence of Eu_2O_3 on the physical, structural, optical and luminescence properties of the zinc bismuth borate glasses. This useful information about the local structure around Eu^{3+} ion can be obtained quite easily from its f-f transition spectra. Since the ground $^7F_0$ level and the first excited $^5D_0$ level of Eu^{3+} ions are non-degenerate (j = 0) under any symmetry, information regarding the local environment around Eu^{3+} ion depends only on the split tings of $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) transitions. Depending on the number of Stark components into which $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3, 4) emission transitions split, the symmetry at Eu^{3+} ion site can be estimated by the crystal-field (CF) parameterization [37].With the composition of the glass, the local environment of the rare earth ions incorporated into the glass network can be changed, leading to local ligand field in homogeneities. The study of such glasses with various spectroscopic techniques will give valuable information on these systems [38].

1.2 Motivation

Nowadays zinc bismuth borate glasses are suitable as gamma ray shielding material, packing of radioactive sources etc.. Enhancing radiation shielding capabilities of this material is an important issue. The first purpose of this research is to explain the shielding behavior of ZBB glasses. Therefore, mass attenuation coefficients, effective atomic numbers and effective electron densities were investigated. In addition, the physical, structural, optical and luminescence properties were then investigated. From the view of application, glasses doped with Eu^{3+} ion have been used in optical devices, field emission technology, phosphors and LEDs which exhibit red emission with higher luminescence efficiency [39] and recently, it can be candidate on scintillation materials [40]**.** From literature reviews, no earlier report on Eu^{3+} ion doped in ZBB glasses. The second purpose of this research is to studies Eu^{3+} ion doped in ZBB glasses were prepared and investigate their physical, structural, optical and luminescence properties.

1.3 Objectives

The objectives of this dissertation are the following

1.3.1 To prepare the zinc bismuth borate glass system of formula (in mol %) xBi_2O_3: 10ZnO: (90 - x) B_2O_3 (where x = 15, 20, 25 and 30 mol %).

1.3.2 To investigate the mass attenuation coefficient, effective atomic numbers, electron densities and some basic radiation shielding parameters of prepared glass samples.

1.3.3 To prepare Eu^{3+} ion doped in zinc bismuth borate glasses of formula (in mol %) (60 - x) B_2O_3: $30Bi_2O_3$: 10ZnO: xEu_2O_3 (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 mol %).

1.3.4 To characterize the physical, structural, optical and luminescence properties of Eu^{3+} ion doped in zinc bismuth borate glasses.

1.4 Thesis Significance

This research will be valuable for further basic studies in the glass science particularly the application of the rare earth doped glass for optical applications. Additionally, this dissertation can lead and encourage other fields of improvement in photonics (photonics: includes the generation, emission, transmission, modulation, signal processing, switching, amplification, detection and sensing of light).

1.5 Literature Reviews

Sha, et al. [41] studied the luminescence of Eu^{3+} ions in heavy metal glass, zinc lead borate glass samples containing various concentrations of Eu^{3+} and Tb^{3+} ions. To study the Tb^{3+} to Eu^{3+} non-radiative energy transfer phenomena. Energy level structures of Tb^{3+} and Eu^{3+} ions were plotted to show the excitation and energy transfer routes. Efficient energy transfer from Tb^{3+} to Eu^{3+} was observed and studied qualitatively in terms of doping concentrations. The sensitization turned out to be less effective than expected. Further studies to characterize the oxidation of Tb^{3+} into tetravalent state and to examine the mechanism of energy transfer are proposed.

Shashidhar, et al. [42] reported the glasses with composition (70-x)Bi_2O_3 - xLi_2O - 30(ZnO -B_2O_3) where ($0 \leqslant x \leqslant 20$) preparation by using melt quench technique. DSC studies showed that the glass transition temperature increases with Bi_2O_3 content. Optical absorption spectra of the pure glasses revealed that the cut off wave length increased and optical band gap energy decreased with increase in Bi_2O_3 content. Electron paramagnetic resonance (EPR) and optical absorption studies of zinc bismuth based glasses were made by introducing Cu^{2+} as a spin probe. It is observed that the spin - Hamiltonian parameters calculated from the EPR spectra are influenced by the glass composition. The Cu^{2+} ions are in well - defined axial sites but subjected to small distortion leading to the broadening of the spectra. The spin-Hamiltonian parameter values indicate that the ground state of Cu^{2+} is $d_{x^2-y^2}$ and the site symmetry around Cu^{2+} ions is tetragonally distorted octahedral. The optical absorption spectra exhibited a broad band corresponding to the d-d transition bands of Cu^{2+} ion. By correlating EPR and optical absorption data, the bond parameters are evaluated and correlated with the optical basicity of the glasses obtained from various techniques.

Shiv, et al. [43] studied the electron paramagnetic resonance, transmission electron microscopy (TEM), optical absorption and photoluminescence (PL) spectroscopic measurements of Mn^{2+}doped high bismuth containing zinc bismuth borate glasses. TEM images reveal homogeneously dispersed Bio Nano particles (NPs) of spherical shape with size about 5 nm. EPR spectra exhibit predominant signals at $g \approx 2.0$ and 4.3 with a sextet hyperfine structure. The resonance signal at $g \approx 2.0$ is due to Mn^{2+} ions in an environment close to octahedral symmetry, where as the resonance at $g \approx 4.3$ is attributed to the rhombic surrounding of the Mn^{2+} ions. The hyperfine splitting constant (A) indicates that Mn^{2+} ions in these glasses are moderately covalent in nature. The zero - field splitting parameter D has been calculated from the allowed hyperfine lines. The optical absorption spectrum exhibits a single broad band centered at 518 nm (19,305 cm^{-1}) is assigned to the ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}$ (G) transition of Mn^{2+} ions. The visible and near infrared (NIR) luminescence bands at 548, 652 and 804 nm have been observed when excited at 400 and 530 nm, respectively. These luminescence centers are supposed to be caused by the lower valence state of bismuth, such as Bi^{2+} and Bi^{+} ions, generated during melting process.

Rajyasree, et al. [44] studied the optical absorption, EPR, FTIR and photoluminescence of modifier oxide and CuO in the glass matrix. A red shift of the absorption band corresponds to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions from P2 to Z4 samples and the increase of hyperfine splitting factor ($A\|$) from P2 to Z2 shows that with the integration of PbO by ZnO the electron density around copper ion are increased. It is also supported by the gradual increase in theoretical optical basicity values of ZnO mixed glasses, as compared to that of PbO mixed glass matrix. Reduced bismuth radicals are found in undoped and 0.4 % CuO doped glasses of both the series. Analysis of the absorption and emission studies indicates that the concentration of luminescence centers of bismuth ions (Bi^{3+} ions in UV region) is decreased by the integration of ZnO as well as by increasing the dopant concentration. In lead series PbO_4 and BiO_3 units are increased from P2 to P4 and in zinc series BiO_3 units are decreased from Z0 to Z4. The conductivity of the glass matrices is increased in both the series with the dopant of CuO.

Atul, et al. [45] investigated and the results are reported the photoluminescence properties of Bi^{3+} co - doped Eu^{3+} containing zinc borate glasses. Bright red emission due to a dominant electric dipole transition ${}^5D_0 \rightarrow {}^7F_2$ of the Eu^{3+} ions has been observed from these glasses. The nature of Stark components from the measured fluorescence transitions of Eu^{3+} ions reveal that the rare earth ions could take the lattice sites of Cs or lower point symmetry in the zinc borate glass hosts. The significant enhancement of Eu^{3+} emission intensity by 346 nm excitation (${}^1S_0 \rightarrow {}^3P_1$ of Bi^{3+} ions) elucidates the sensitization effect of co - dopant. The energy transfer mechanism between sensitizer ($Bi^{3+)}$ and activator (Eu^{3+}) ions has been explained.

Inder, et al. [46] investigated the optical absorption and fluorescence spectra of Pr^{3+}ions doped zinc borate glasses with varying concentration of bismuth oxide. The Judd - Ofelt intensity parameters Ω_λ ($\lambda = 2, 4, 6$) and other radiative properties like radiative transition probability, radiative life time, branching ratio and stimulated emission cross-section of the prepared glasses have been calculated. The variation of Ω_2 with Bi_2O_3 content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in their rare earth oxygen (RE - O) covalency. The branching ratio for $^3P_0 \rightarrow {}^3F_2$ transition is 42% and the predicted spontaneous radiative transition probability rates are fairly high (14,347 - 14,607 s^{-1}). This is beneficial for lasing emission. The stimulated emission cross-section for all the emission bands has been calculated.

Agarwal, et al. [47] studied the optical absorption and fluorescence spectra. Judd - Ofelt approach has been applied for the $f \leftrightarrow f$ transition of Sm^{3+}ions to evaluate various intensity parameters (Ω_2, Ω_4, Ω_6). The variations in intensity parameters, radiative transition probabilities and hypersensitive band positions with composition have been discussed. The variation of Ω_2 with Bi_2O_3 content have been attributed to change in the asymmetry of the ligand field at the rare earth ion site and to the changes in their rare earth-oxygen covalency, whereas the variation of Ω_6 is found to be strongly dependent on nephlauxetic effect. The shift of the hypersensitive band shows that the covalency of the RE-O bond increases with increase of Bi_2O_3 content due to increased interaction between the Sm^{3+}ion and non - bridging oxygens. The radiative transition probabilities for the Sm^{3+}ions are large in zinc bismuth borate glasses, suggesting their suitability as laser material.

Maria, et al. [48] prepared and later thermally treated the glasses with composition $xEr_2O_3(100 - x)[72Bi_2O_3 \cdot 25PbO \cdot 3Ag_2O]$ where x = 0 - 20 mol%. The local environments characteristic of this system were investigated using X - ray diffraction and FTIR spectroscopy. The results show that the glass or glass ceramic network structure resembles to that of the host matrix, being composed of $[BiO_3]$, $[BiO_6]$, $[PbO_3]$ and $[PbO_4]$ structural units. The addition of Er_2O_3 stabilizes the host glass or glass ceramic structure. The erbium ions play the role of a network modifier in the studied glasses. It was shown that the heat treatment at 650 °C leads to the crystallization of the Bi_2O_3 and $PbO_{1.44}$ phases.

Sooraj, et al. [49] studied the absorption and emission spectra of the Ho^{3+} ion doped lead-zinc-borate glasses in the composition (mol %) of $(20 - x)PbO - 20ZnO - (59 + x) B_2O_3 - 1.0Ho_2O_3$ where x = 0, 5, 10, 15 of PbO content with $\lambda_{exc} = 405$ nm. The experimental absorption band energies have satisfactorily been correlated with the theoretical results with an r.m.s deviation of zero with the following correction factors obtained by a least square fit analysis: $\Delta E^1 = 348.495936\ cm^{-1}$, $\Delta E^2 = 1.436043\ cm^{-1}$, $\Delta E^3 = 46.481575\ cm^{-1}$, $\Delta\xi 4f = -\ 28.512979\ cm^{-1}$, $\Delta\alpha = 55.508936\ cm^{-1}$, $\Delta\beta = -\ 1394.339908\ cm^{-1}$ and $\Delta\gamma = 1208.424336\ cm^{-1}$. By applying the Judd-Ofelt intensity parameter Ω_2 has been found to be linearly decreasing with the PbO content from 5 to 10 mol% and then increasing. And also radiative (A, AT, β, τ_r) characteristic factors of the luminescent transitions ($^5I_8 \leftarrow {}^5F_{3,\,4,\,5}$ and $^5S_2$) of the glasses have been evaluated. Stimulated emission cross-sections (σ_p^E) of the measured emission transitions of holmium glasses have also been computed.

Kam, et al, [50] reported the development and luminescence performance of a new family of optical glasses containing Eu^{3+} (1 mol %) in the chemical composition of $75Bi_2O_3$ - $21B_2O_3$ - $4R_2O$ (where R = Li, Na & K). We have also investigated the different physical and non-linear properties and zero material dispersion wavelength of the reference glasses without the dopant Eu^{3+} and the results are presented. Under an UV source, especially with Li^+ added, Eu3^{+}: glass displayed a bright red emission at 614 nm ($^5D_0 \rightarrow {}^7F_2$). Among the different excitation bands, $_7F^0{}_5L^6$ (392 nm) is a spin allowed transition which prominently demonstrates stronger emissions of $^5D_0 \rightarrow {}^7F_0$ (578 nm); $^5D_0 \rightarrow {}^7F_1$ (593 nm); $^5D_0 \rightarrow {}^7F_2$ (614 nm); $^5D_0 \rightarrow {}^7F_3$ (654 nm); $^5D_0 \rightarrow {}^7F_4$ (688 nm); $^5D_0 \rightarrow {}^7F_5$ (702 nm); from all three glasses. The emission process has been explained by means of an energy level scheme.

Elfayoumi, et al [51] studied the absorption and emission spectra of Sm^{3+} and Eu^{3+} co - doped lithium borate glass with composition $xSm_2O_3 + (100\text{-}x)[0.84H_3BO_3 + 0.15Li_2O + 0.01Eu_2O_3]$, where x = 0.0, 0.1, 0.2, 0.5, 0.6 and 0.7 mol %. The concentration of Sm^{3+} was varied keeping the Eu^{3+} concentration fixed at 0.01 mol %. The optical absorption and emission spectra have been measured in the spectral range from 350 to 2400 nm. The oscillator strength, Judd - Ofelt intensity parameters, branching ratios and radiative transition probabilities were calculated. The obtained results are discussed and compared with other literature data for Eu^{3+} in various compounds.

Lakshminarayana, et al. [52] reported the reddish orange and green luminescent Eu^{3+} and Tb^{3+} of B_2O_3 – ZnO - PbO glasses, that have been developed to investigate their spectral properties from the measurement of their XRD, DSC, absorption, excitation and emission profiles. Direct and indirect optical band gaps have been calculated based on the glasses UV absorption spectra. The photoluminescence spectrum of Eu^{3+} has shown five emission transitions ($^5D_0 \rightarrow {}^7F_{0\text{–}4}$) at 579 nm, 591 nm, 614 nm, 653 nm and 703 nm with excitation wavelength at 392 nm ($^7F_0 \rightarrow {}^5L_6$). Similarly Tb^{3+} has revealed four emission bands ($^5D_4 \rightarrow {}^7F_{6,\,5,\,4\text{ and }3}$) at 489 nm, 543 nm, 587 nm and 623 nm with 377 nm ($^7F_6 \rightarrow {}^5G_6$) as the excitation wavelength. Upon exposure to an UV source (254 nm), Eu^{3+} or Tb^{3+} of BZP glasses have shown bright reddish orange or strong green colours.

Lourenco et al. [53] investigated the Eu^{3+} doped lead borosilicate glasses (SiO_2 - B_2O_3 - PbO_2) synthesized by fusion method. They investigated optical properties as a function of temperature. Atomic Force Microscopy images obtained for a glass matrix annealed at 350 and 500 °C show a precipitated crystalline phase with sizes 11 and 21 nm respectively. Besides as the temperature increases from 350 to 300 K a strong Eu^{3+} photoluminescence (PL) enhancement takes place. This anomalous feature is attributed to the thermally activated carrier transfer process from nanocrystals and charged intrinsic defects states to Eu^{3+} energy levels. In addition, the PL peaks in this temperature range were assigned to the Eu^{3+} transitions $^5D_0 \rightarrow {}^7F_2$, at 612 nm, $^5D_0 \rightarrow {}^7F_1$, at 595 nm and $^5D_0 \rightarrow {}^7F_0$ at 585 nm. It was also observed that the $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ PL bands at 655 and 700 nm respectively show a continuous decrease in intensity as the temperature increases.

Chonggeng et al. [54] studied the Ce^{3+}, Eu^{3+} and Tb^{3+} singly doped and Ce^{3+}/Eu^{3+} and Ce^{3+}/Tb^{3+} co-doped zinc phosphate glasses. The samples were prepared by sintering P_2O_5, ZnO, $Ce_2(C_2O_4)_3 \cdot 10H_2O$ and Eu_2O_3/Tb_4O_7 mixtures at 1200 °C in the air for 2 h and then annealing at 450 °C for 10 h. The obtained glasses were homogeneous and transparent.

The glasses without Ce^{3+} were colorless and those with Ce^{3+} showed slightly yellow. The singly doped glasses showed strong emissions and excitations from doped trivalent rare earth ions. Strong energy transfer from Ce^{3+} to Tb^{3+} was observed for Ce^{3+} / Tb^{3+} coped samples. There were also some very weak evidences for the energy transfer from Ce^{3+} to Eu^{3+}.

Stambouli et al. [55] investigated the structural, thermal and optical properties of Eu^{3+} doped TeO_2 - La_2O_3 - TiO_2 glass. The differential scanning calorimetry (DSC) measurements reveal an important stability factor $\Delta T = 143.52$ K, which indicates the good thermal and mechanical stabilities of tellurite glass. From the absorption spectrum, the optical band gap was found to be direct with $E_g = 3.23$ eV. The temperature dependences of photoluminescence (PL) properties of Eu-doped and Eu-Tb co-doped tellurite glass are investigated. As the temperature increases from 7 to 300 K, both the PL intensity and the PL lifetime relative to the $^5D_2 \rightarrow {}^7F_0$ are nearly constant below 230 K and then an enhancement takes place. This anomalous feature is attributed to the thermally activated carrier transfer process from charged intrinsic defects states to Eu^{3+} energy levels.

Surendra et al. [56] reported the phosphate ($P_2O_5 + K_2O + BaO + Al_2O_3 + Eu_2O_3$) and fluorophosphate ($P_2O_5 + K_2O + BaO + BaF_2 + Al_2O_3 + Eu_2O_3$) glasses with different Eu^{3+} ion concentrations. The samples have been prepared and characterized through optical absorption, photoluminescence and decay times. An intense red luminescence is observed from the $^5D_0$ emitting level of Eu^{3+} ions in these glasses. The relative luminescence intensity ratio of $^5D_0 \rightarrow {}^7F_2 \rightarrow {}^5D_0 \rightarrow {}^7F_1$ transitions has been evaluated to estimate the local site symmetry around the Eu^{3+} ions. The emission spectra of these glasses show a complete removal of degeneracy for the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions. Second and fourth rank crystal field (CF) parameters have been calculated together with the CF strength parameter by assuming the C_{2v} symmetry for the Eu^{3+} ions in both the phosphate and fluorophosphate glasses. Judd-Ofelt parameters have been evaluated from the luminescence intensity ratios of $^5D_0 \rightarrow {}^7F_J$ (J = 2, 4 and 6) to $^5D_0 \rightarrow {}^7F_1$ transitions. These parameters have been used to derive radiative properties such as transition probabilities, branching ratios, radiative lifetimes and peak stimulated emission cross-sections for the $^5D_0 \rightarrow {}^7F_J$ transitions. Decay curves of the $^5D_0$ level of Eu^{3+} ions in these two Eu^{3+}: glass systems have been measured by monitoring the $^5D_0 \rightarrow {}^7F_2$ transition (611 nm) at room temperature. The experimental lifetime of the $^5D_0$ level in the title glasses is found to be higher than Eu^{3+} doped niobium phosphate glasses. The analysis indicates that the lifetime of the $^5D_0$ level is found to be less sensitive to the Eu^{3+} ion concentration and addition of BaF_2 has no significant effect on the optical properties of Eu^{3+} doped phosphate glasses.

Fengxia et al. [57] studied the Eu doped transparent oxyfluoride borosilicate glass ceramics containing Ba_2GdF_7 nanocrystals, that were prepared by controlling crystallization of melt quenched glass fabricated under a reductive atmosphere. In the oxyfluoride borosilicate glass ceramics, the mean crystal size of Ba_2GdF_7 nanocrystals was about 30 nm, which could be observed by X - ray diffraction (XRD) and transmission electron microscopy analysis. The photoluminescence spectra of the samples excited at 392 nm showed that, besides the characteristic sharp emissions of Eu^{3+} ions, a very intense broadband emission of Eu^{2+} ions centered at 450 nm appeared. The photoluminescence intensity of Eu^{3+} and Eu^{2+} ions in the glass ceramics was much stronger than that in the as-made precursor.

The long decay lifetimes of Eu^{3+} and Eu^{2+} ions evidenced the partitions of Eu^{3+} and Eu^{2+} ions into the Ba_2GdF_7 nanocrystals. The energy transfer from Gd^{3+} ions to Eu^{3+} and Eu^{2+} ions was confirmed by the excitation and emission spectra.

Sabikoglu et al. [58] reported the structural and photoluminescence of lithium metasilicate (Li_2SiO_3) phosphor ceramics doped with four rare earth ions. X - ray diffraction patterns show a dominant phase, characteristic of the orthorhombic structure Li_2SiO_3 compound and the presence of dopants has no effect on the basic crystal structure of the material. The first excited state Er^{3+} luminescence at 1.54 μm arises from a sharp atomic - like radiative transition between the $^4I_{13/2}$ state and the $^4I_{15/2}$ state (ground level) under a 532 nm line of an Ar ion laser excitation. Sm doped samples showed Sm^{3+} emission characteristics corresponding to the some $^4G_{5/2} \rightarrow {}^6H_j$ (j = 5/2, 9/2, 11/2) transitions indicating a strong crystal-field effect. PL spectra of Eu doped material exhibited peaks corresponding to the $^5D_0 \rightarrow {}^7F_j$ (j = 0, 1, 2, 3 and 4) transitions under 405 nm excitation. The dominant red color emission at 612 nm from the hypersensitive ($^5D_0 \rightarrow {}^7F_2$) transition of Eu^{3+} indicates the inversion antisymmetry crystal field around Eu^{3+} ion, which is favorable to improve the red color purity. Dy doped samples showed the Dy^{3+} emission characteristic due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Their relative intensity ratios also suggested the presence of a symmetric environment around the metal ion. We suggest that lithium metasilicate has enough potential candidates to be a phosphor material.

Dongpu et al. [59] studied the emission spectra of Eu^{3+}: CaO - La_2O_3 - B_2O_3 glass. From the measurement of its optical absorption spectrum, three phenomenological Judd-Ofelt intensity parameters have been computed and used to parameterize the radiative properties such as spontaneous emission probability (A), radiative rate (AT), radiative lifetime (τ_R), branching ratios (β) and stimulated emission cross sections of the measured emission transitions. A significant change has been observed in the fluorescence features of Eu^{3+} glass due to the occurrence of crystallization from the controlled heat treatment schedules. Local environment structure in the glass around the rare earth ion has also been understood. From the XRD spectral profiles of the ceramized Eu^{3+}: calcium lanthanum borate glass, the crystalline phases have been analyzed in correlation with the measurement of FTIR spectra of this red luminescence glass.

Table 1.1 Summary and Literature Reviews.

Glasses system	**Properties**				**Ref**
	Physical Properties	**Structural Properties**	**Optical Properties**	**Luminescence Properties**	
50 B_2O_3, 30 ZnO, 15 PbO, x Eu_2O_3, y Tb_4O_7 and (5-x-y) in mol%	–	–	–	● photoluminescence	[41]
$(70-x)Bi_2O_3-xLi_2O-30(ZnO-B_2O_3)$	● Glass transition temperature	● EPR	● UV-Visible	● Judd-Oflet Analysis	[42]
$23B_2O_3-5ZnO-72Bi_2O_3-xMnO_2$ (where x = 0, 0.0012, 0.003and0.0058 wt %)	● TEM	● EPR ● NPs	–	● photoluminescence	[43]
10MO. 20Bi_2O_3 (70-x) B_2O_3.xCuO [M = Pb, Zn] with x = 0, 0.4 and 0.8(wt %)	–	● EPR ● FTIR	● UV-Visible	● photoluminescence	[44]
$60ZnO-(40-x)B_2O_3-0.2Eu_2O_3-xBi_2O_3$ (x = 0, 0.1,0.2,0.5,1.0) mol%	–	–	–	● photoluminescence	[45]
$20ZnO\cdot xBi_2O_3\cdot (79.5-x) B_2O_3\cdot 0.5Pr_2O_{11}$ (15≤x≤35 x in mol %)	–	–	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis	[46]
20ZnO.xBi_2O_3.(79- x)B_2O_3.1Sm_2O_3, (15≤x≤35 x in mol %)	–	–	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis	[47]
$xEr_2O_3(100-x)[72Bi_2O_3\cdot 25PbO\cdot 3Ag_2O]$	–	● XRD ● FTIR	–	–	[48]
$(20-x)PbO-20ZnO-(59+x)B_2O_3-1.0Ho_2O_3$	–	–	–	● photoluminescence ● Judd-Oflet Analysis	[49]
$75Bi_2O_3-21B_2O_3-4R_2O$ (where R = Li, Na & K)	–	–	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis	[50]
$xSm_2O_3+(100-x)[0.84H_3BO_3+0.15Li_2O+0.01Eu_2O_3]$	–	–	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis	[51]
$B_2O_3-ZnO-PbO$	● DSC	● XRD	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis	[52]

Table 1.1 Summary and Literature Reviews (cont'd).

Glasses system	**Properties**				**Ref**
	Physical Properties	**Structural Properties**	**Optical Properties**	**Luminescence Properties**	
SiO_2-B_2O_3-PbO_2	–	● AFM	–	● photoluminescence	[53]
zinc phosphate glasses)	–	–	● UV-Visible	● photoluminescence	[54]
TeO_2-La_2O_3-TiO_2	● DSC	–	–	● photoluminescence	[55]
P_2O_5+K_2O+BaO+Al_2O_3+Eu_2O_3) and (P_2O_5+K_2O+BaO+BaF_2+Al_2O_3+Eu_2O_3	–	–	● UV-Visible	● photoluminescence ● Judd-Oflet Analysis ● Decay time	[56]
borosilicate glass ceramics containing Ba_2GdF_7	● TEM	● XRD	–	● photoluminescence	[57]
lithium metasilicate (Li_2SiO_3) phosphor ceramics doped with four rare earth (RE)	–	● XRD	–	● photoluminescence	[58]
Eu^{3+}: CaO-La_2O_3-B_2O_3	–	● XRD ● FTIR	● UV-Visible	● Judd-Oflet Analysis	[59]