The Excitation dependent luminescence properties of Sm^{3+} barium borate glass

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ABSTRACT
Sm^{3+}doped barium borate glass ($60B_2O_3$ + $39.7BaCO_3$ + $0.3Sm_2O_3$) wassynthesizedand studiedbyvarious spectroscopic techniques. UV-absorption data were used to calculate the Urbach energy (E_u) and optical band gap energies (E_g) of the glasses. In this work, the excitation-dependent photoemission properties of the prepared glass were studied. The photoluminescence (PL) spectraexhibits the radiative transitions inSm^{3+} barium borate (SBB) glass and the radiative transitions of Sm^{3+} ions from $^4G_{5/2}$ to $^6H_{9/2,}{}^6H_{7/2}$, and $^6H_{5/2}$, attributes in the emissions at 649, 602, and 566 nm. The PL decay study with the Inokuti-Hirayama model, indicates the different multipolar interaction mechanism.The study determines critical transfer distance(R_c), the energy transfer parameter (Q), and donor-acceptor interaction parameter (C_{DA}). The thermoluminescence (TL)kinetic parameters of glass were studied by the peak shape method. From the PL spectra, colorimetric parameters were evaluated, shows the glass could be used for various optoelectronic applications.

Keywords: Barium borate glass, Urbach energy, photoluminescence, chromaticity coordinates, correlated color temperature (CCT)

INTRODUCTION

Recently Glass is well-known for its numerous applicationsin science and technology, which have paved the way for the development of innovative glass. The chemical composition, kind of bond, structure, and synthesis mechanism all influence the physical properties of the glass. Rare earth-doped glass draws great interest among researchers due to its appealing optical features and excellent luminescence efficiency [1-4]. Among the networker formers, B_2O_3 has been the primary choice due to its physical, structural, and optical advantages over other conventional network formers. Another exceptional quality of borate glass is its great transparency, low melting point, and high thermal stability [5-7].The assembly of di, tri and tetra borates was credited with the construction of a more stable three dimensional network. The nonlinear and other characteristics of the glass are determined by the chemical compositions in the glass system.Modification made by the inclusion of alkali or alkaline-earth cation content produce mixed alkali effects, which hold certain significance in the literature[6, 8].Heavy metal oxide in borate glasses have distinct interest due to their unique properties and their potential stability. In glasses, barium works as a former in high concentrations and as a modifier in low concentrations. Barium-based glasshasrelatively low melting points, low thermal expansion coefficients, low dispersion, high refraction, and high electric resistance. Aly saeed et al. [8]observed that ahigh BaO concentration in the BaO-ZnO-MgO-Na2O-Li2O-B_2O_3 glass system resulted in the formation of non-binding oxygen bond, which has a significant influence on the optical band gap and Urbach energy values, as well as increases refractive index and electronic polarizability. Kirdsiri et al. investigated the optical properties of glasses with different alkaline earth metal as modifier oxides, the structural and optical charcteristics of barium incorporated glass shows better results than other alkaline earth metal, they also stated barium incorporated glasses are better host for solid state applications [6]. Trivalent samarium ions emit a strong orange-red lightand have potential applications in color displays, UV-sensor, laser andhigh-density optical storage [7, 9, 10]. The light bright shade of red emission was attributed to the electronic transitions $^4G_{5/2}$ to$^6H_{9/2}$, $^6H_{7/2}$, and$^6H_{5/2}$in the inorganic lattice of Sm^{3+} ion-doped materials.The spectroscopic, structural and luminescence characteristics of Sm^{3+} ions have already been investigated in

various hosts [1, 3-7]. In the present work, the structural, optical, and luminescence properties of the B_2O_3-BaO-Sm_2O_3 glass system were studied.

Materials Synthesis

The Conventional melt quenching process is used to synthesis barium borate glass sample, with boron oxide (B_2O_3) actingas network former and barium carbonate ($BaCO_3$)as network modifier. The network modifier-to-network former ratio is fixedat 2:3. $60B_2O_3$ + $39.7BaCO_3$+ $0.3Sm_2O_3$ (SBB), the chemicals are weighed, carefully mixed, and melted at 1170 °C for approximately 8 hours in an alumina crucible. To avoid thermal shock, a brass mould was preheated to 380°C and the molten mixture at 1170 °C was transferred and quenched. To eliminate the residual mechanical and thermal stress that arose during subsequent cooling, the transferred mixture was annealed at 450°C for 2 hours. The annealed sample is cooled gradually to ambient temperature, and crushed down to fine powder for further characterization.

Structural properties

The FTIR spectra of SBB glass was shown in Fig.1, determined in the spectral range of 500 to 3500 cm^{-1}.Broad peakat 1365 cm^{-1}corresponds to the asymmetric stretchinginBO$_3$ structural unit. The peakpositioned at 1202 cm^{-1} is most likely due to the B–O stretching vibration of trigonal BO_3 units in theboroxol rings. The presence of B–O stretching in tetragonal BO_4 units is attributed to a peak at 928cm^{-1} obtained in the glass network. The peaks at 928 and 1365 cm^{-1} confirms the SBB glass network structure contains both tetrahedral and trigonal borate units respectively, barium oxide could have promote in the conversion of some triangular borate group into tetrahedral borate group[11]. The peak at 706 cm^{-1}confirms the bending of B-O–B linkage within the borate network[12]. The specific low intensity vibration by Ba–O bonds wereconfirmed by peak at 526cm^{-1}. The peaks 2114, and 2325 cm^{-1}attributes to vibration of water, hydroxyl (OH) group.

The Raman spectra SBB glass was found to be asymmetric as shown in Fig. 2. This asymmetric nature of Raman bands is due to the superimposition of several bands with different line parameters. FT-Raman spectra were recorded for SBB glass confirms thestructural and functional groups in the sample. The spectra in the 500-2000 cm^{-1}range were obtained using a Bruker RFS-7 (SAIF, IITM) Raman spectrometer. The peak at 747 cm^{-1} is due toγ-vibrations of $[BO_3]^{3}$. The Penta-borate vibrations are confirmed at 966 cm^{-1}. The peak positioned at 1441 cm^{-1} ascribed to B–O–B stretching in the glass network.All the vibrational peaks in both the spectra were tabulated in Table. 1, the peaks assigned wereshows good match when compared with the literature values.

Optical Properties

Fig 3. Shows the transmittance spectra recorded using PEL-900-UVNS spectrometer in 200 – 1200 nm range, the SBB glassexhibiting approximately 75 % transmittance in the 400 – 1200 nm range.The presence of small intensive peaks in distinct location at 407 nm and 956 nm in the SBB glass are ascribed to the Sm^{3+} ion $^6H_{5/2} \rightarrow {}^6P_{3/2}$ and $^6H_{5/2} \rightarrow {}^6F_{11/2}$ transition, respectively. Mott et al. [13] established a relationship between the photon energy and optical absorption coefficient (α).

$$\alpha(\nu) = \frac{B}{h\nu}\left(h\nu - E_g\right)^n \qquad (1)$$

Where, B is the absorption constant, n is the power factor,E_g represents the band-gap energy.For allowed direct transition n value is ½, and for indirect transition value is 2. Fig.4representdirect and indirect band gap energy. For SBB glass, the calculated direct and indirect E_g values were3.35 eV and 2.21 eV, respectively. The lack of non-binding oxygens (NBOs) reduces polarizability and increases the optical band-gap energy of the glass, as the NBOs bind an excited electron less strongly than binding oxygen (BOs), making NBOs more polarizable than BOs. However, the existence of heavy metal ions (Ba^{2+}) results in increase in the amount of free electronsin the glass network. This caused electrons to agglomerate in low energy levels, contributing to the decrease in the band-gap energy.

The Urbach energy (E_u)value were calculated from UV-absorption data.Fig.5. depicts the response of ln(α) vshν, the E_u is calculated using the Urbach empirical rule[14]and the reciprocal slopes of the linear fit.

$$\alpha(\nu) = \alpha_o \exp\left(\frac{h\nu}{E_u}\right) \qquad (2)$$

The E_u values for the SBB glass was found to be 3.315 eV. Saeed et al. reported inclusion of BaOin the glass system changes the band gap and urbach energy [8]. Both E_g and $E_u$values are inversely related, higher E_u indicates surge in bonding defects and NBO atoms in the glass. The higher concentration of BaO in the SBB glass system increases the degree of electron localization, and donor centers.

Photoluminescence

Luminescence spectra of the Sm^{3+} barium borate glass was recordedat room temperature by using a F-900fluorescence spectrometer. The PLE spectra of SBBglass when observed at 603nm was shown in Fig. 6, the excitation peaks at 348, 365, 378, and 407 nm, wereascribed to the transitions from $^6H_{5/2} \rightarrow {}^4H_{9/2}$, $^6H_{5/2} \rightarrow {}^4D_{3/2}$, $^6H_{5/2} \rightarrow {}^4P_{7/2}$, and$^6H_{5/2} \rightarrow {}^4P_{3/2}$ respectively. The excitation peaks in 233 nm region wasattributable to charge transfer state of Sm^{3+} ion, a2p orbital electron of oxygen is transferred to 4f orbital of samarium. The excitation peaks at 348,365, 378 and 407 nm are due to the f-f transition of Sm^{3+} ions.Theexcitation dependent PL emission spectra of SBB glass were recorded for the excitation wavelengths of 233, 254 and 407 nm. The electrons in Sm^{3+} ions excited from the$^6H_{5/2}$ground state to$^4F_{5/2}$ the excited state and then fall back to the $^4G_{5/2}$ state swiftly by nonradiative relaxation. The emission observed at 566, 602, and 649 nm were corresponds to radiative transitions of Sm^{3+} ions from$^4G_{5/2} \rightarrow {}^6H_{5/2}$ (magnetic dipole allowed transition (ΔJ = 0)),$^4G_{5/2} \rightarrow {}^6H_{7/2}$ (either electric dipole or magnetic dipole character) and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (mainly of electric dipole (ΔJ = ±1) allowed transition) respectively. In general, the intensity ratios ofelectric and magnetic dipolesdetermine the symmetry of the environment surounding the Sm^{3+} ion.In SBB glass possess more asymmetric nature as $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition is more intense than the magnetic dipole transition.Apart from the radiative and multi-phonon relaxation there may take place also the donor-donor (DD) relaxations and donor-acceptor (DA) responsible for cross relaxation leading migration of excitation energy. The cross relaxation (CR) channels witnessed between the donor and acceptors of Sm^{3+} ion are shown in the Fig.7. The CR1 was laid between$^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{11/2} + {}^6F_{5/2,}$ CR2 was laid between $^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{7/2} + {}^6F_{9/2}$ and the CR3 was laid between $^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_{5/2} + {}^6F_{11/2}$. In CR1, the Sm^{3+} ion in the $^4G_{5/2}$ level relaxes to $^6F_{11/2}$ level and excites aneighbor Sm^{3+}ions from $^6H_{5/2} \rightarrow {}^6F_{5/2}$ level, because the difference in energy of the two related transitions matches narrowly.

PL Decay

The PL decay of $^4G_{5/2} \rightarrow {}^6H_{7/2}$ of Sm^{3+} ion in SBB glass has been investigated for excitation wavelengths 233 nm and 407 nm, the intensity verses time curves are depicted in Fig. 8. From the decay curve, experimental lifetime value for the SBB glass were evaluated. The PL decay curve can be fitted by the following third-order exponential function as[15]:

$$I(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right) + A_3 \exp\left(\frac{-t}{\tau_3}\right) \quad (3)$$

Here, I(t) signifies fluorescence intensity; t represents the time; τ_1, τ_2 and τ_3 denotes decay times; A_1, A_2 and A_3 are constantsfor the exponential components. The three exponential decay shows that more than one decay channel is intricate in the total decay process. The average lifetime (τ_{av}) calculatedwith the following equation:[16]

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \quad (4)$$

To determine the dominantmulti-polar interaction, theInokuti-Hirayama (I-H) model was used to investigate the non-single exponentialPL Decay curve [17, 18].

$$\phi(t) = A.\exp\left[-\frac{t}{\tau} - Q\left(\frac{t}{\tau}\right)^{3/S}\right] \quad (5)$$

S isentirely dependent on the type of multi-polarinteraction, withS=6, for dipole-dipole (D-D) interaction. For the S=8, and 10 corresponding to dipole-dipole (D-D), dipole-quadrupole (D-Q) and quadrupole-quadrupole (Q-Q) interactions, respectively. The Probability of the energy transfer(Q) is calculated through fitting process. The critical interaction distance (R_c) is the distance of separation between donor and acceptor for which the energy transfer rate is equal to donor intrinsic decay rate ($1/\tau_0$). It is correlated with Q as follows

$$Q = \frac{4}{3}\pi\Gamma\left(1 - \frac{3}{S}\right)N_A R_c^3 \quad (6)$$

Here, Γ represents the gamma function. Concentration of $Sm^{3+}$is estimated to be 1.188 x 10^{20} ions/cm^3. $R_c$and $C_{DA}$are the critical distance for various interactions andthe donor-acceptor ions interaction parameter, respectively are given below.

$$R_c = \sqrt[3]{\frac{3Q}{4\pi\Gamma N_A}} \quad (7)$$

$$C_{DA} = \frac{R_c^S}{\tau} \quad (8)$$

$$D_{random} = 2\left(\frac{3}{4\pi N_A}\right)^{1/3} \quad (9)$$

The D_{random} values are found to be 25.2 Åexceed the R_c values. This confirms the cross-relaxationof the RE^{3+} ions. Table 2 shows the calculated values for the probability of energy transfer (Q),critical interaction distance (R_c), donor-acceptor ions interaction parameter (C_{DA}), and average lifetime (τ_{av}). The results reveal that energy transfer between Sm^{3+} ion is predominantly by dipole-dipole electrostatic interactions.

Color chromaticity and color correlated temperatures

For examining the excitation-dependent luminescence of the SBB glass PL spectra were recorded for various characteristic excitation wavelengths (At 233,407 and 254 nm). We could infer from Fig. 9that with the change in Excitation wavelength the intensity of the luminescent band related to Sm^{3+} ion changes. For identifying the accurate color emitted from the glass we can use CIE chromaticity coordinates. The emission spectra for various excitation of Sm^{3+}glasses are evaluated usingCIE coordinates by using color matching function.Colorcorrelated temperature (CCT) describes in more detail the color of radiated light emitted by the luminescent source and is measured in Kelvin (K).McCamy's formula can be used to determine the CCT with a precision of less than two Kelvin.

$CCT = - 68253.3n + 3525n^2 - 449\ n^3 + 5520.33$ (10)

Where $n = (x - x_0)/(y - y_0)$

The color purity of the emitted light was calculated using the following formula[19]

$$P_c = \frac{\sqrt{((x_s - x_i)^2 + (y_s - y_i)^2)}}{\sqrt{((x_d - x_i)^2 + (y_d - y_i)^2)}} \times 100\% \quad (11)$$

The x and y coordinates, CCT and color purity of the SBB glass system were tabulated in Table 3.

Thermoluminescence

It is significant to create large number of trap centers for a certain Thermoluminesce dosimetry (TLD) application, which can be accomplished through appropriate doping to the host material. In a TLD material electrons need be trapped in defects at low temperature and then released by thermal stimulation to give a glow peak. During recombination of the released electrons and hole at luminescence centeremits light (hν). For TLD application, it is essential to examine trap centers andtrap depth. Fig.10depicts TL glow curve of γ-irradiation (~2 kGy)SBB glass recorded using TL1009 (NUCLEONIX TL analyzer). The glow curve's complexity may be because ofsuperimposing of several closely spaced bands of trap depths. Deconvolution of glow curve revels the presence of trap centres at 523 K and 575 K in the irradiated samples. The TL kinetic parameters, such as the frequency factor (s) and activation energy (E)were calculated and studied [20] and the results were given in the Table.4, from the analysis the SBB glassmight be capable material as dosimeter.

CONCLUSION

The synthesized Sm^{3+}doped barium borate glass shows good transmittance of about 75% in the 400 – 1200 nm wavelength range. The E_u values of SBB glass was found to be 3.32 eV. The FTIR and FT Raman spectral studies of the glass ensure the formation of barium and borate groups.The prepared glassesexhibit excitation-tunable emission, which could be clearly seen from the CIE coordinates calculated for the excitation wavelength of 233, 254 and 407 nm. The results of C_{DA} energy transfer microparameter confirms the dipole-dipole interaction to be dominant.The kinetic parameters computed from deconvolution of glow curve show trap center at high temperature capable material for dosimetric applications.The variation in the red emission with excitation of Sm^{3+}doped barium borate glasses could be suitable for tunableLED application.

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Data availability statement

The raw/processed data required to reproduce these findings are shared in the form of tables in the Manuscript itself.

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