Chapter VIII

Summary and suggestions for further work

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8.1. Summary of the results

The major objective of this thesis was to analyze the structural and luminescence behaviour of Sm^{3+}, Eu^{3+} and Dy^{3+}doped heavy metal borotellurite glasses for visible laser and WLED applications. These glasses were synthesized by melt quenching technique. The physical properties such as density, refractive index, dielectric constant, reflection losses, polaron radius and inter-ionic distance have been estimated and listed in the chapter III to VII. Glassy nature of the prepared glasses was confirmed through XRD patterns. FTIR and Raman measurements were used to study the local structure of the prepared glasses. Band positions, direct and indirect band gap, bonding parameter, nephelauxetic ratio, oscillator strength and Judd–Ofelt intensity parameters of the glasses were estimated using absorption spectra. Radiative parameters such as effective bandwidth, transition probability, stimulated emission cross-section, branching ratio and radiative lifetime were calculated through PL emission spectra. Lifetime of an excited state of a rare earth ion was obtained from the luminescence decay curves. The CIE chromaticity coordinates, colour purity and the correlated colour temperature of the rare earth doped glasses have been arrived at from the photoluminescence emission spectra.

8.2. Conclusion

Amorphous nature of all glasses, discussed in the chapters (III to VII) were confirmed though the X-ray diffraction pattern. FTIR and Raman spectra of the prepared glasses reveal the presence of diborates, triborates, tetraborates, pentaborates, orthoborates containing three and four coordinated boron, ring and chain-type metaborate, Te−O, TeO_3, TeO_4 groups, bending vibrations of tetrahedral PbO_4 groups and symmetric stretching vibrations of P−O−P vibration in PO_4 groups. Radiative properties such as, emission band position (λ_P, nm), transition probability (A, s^{-1}), branching ratio (β_R(exp)), effective bandwidth ($\Delta\lambda_{eff}$, nm), stimulated emission cross-section (σ_E^P $\times10^{-21}$ cm^2), experimental lifetime (τ_{exp}, ms), non-radiative decay rate (W_{NR}, s^{-1}), gain bandwidth product ($\Delta\lambda_{eff}\times\sigma_E^P$ ($\times10^{-25}$ cm^{-3})), optical gain ($\tau_R\times\sigma_E^P$($\times10^{-28}$ cm^2s^{-1})) and quantum efficiency (η, %) for prominent emission transitions of Sm^{3+}, Eu^{3+} and Dy^{3+} ions in different glass matrices (from the best glass in each work) is presented in table 8.1. From table 8.1 it is seen that all the prepared glasses possess higher values of branching ratio (> 55 %) and higher values of stimulated emission cross-section.

Table 8.1: Radiative properties emission peak wavelength (λ_P, nm), transition probability (A, s^{-1}), branching ratio (β_R (exp)), effective bandwidth ($\Delta\lambda_{eff}$, nm), stimulated emission cross-section (σ_E^P $\times10^{-21}$ cm^2), experimental lifetime (τ_{exp}, ms), non-radiative decay rate (W_{NR}, s^{-1}), gain bandwidth product ($\Delta\lambda_{eff}\times\sigma_E^P$ ($\times10^{-25}$ cm^{-3})), optical gain ($\tau_R\times\sigma_E^P$ ($\times10^{-28}$ cm^2s^{-1})) and quantum efficiency (η, %) for prominent emission transitions of Sm^{3+}, Eu^{3+} and Dy^{3+} ions in different glass matrices

Glass	Transition	λ_p	A	$\Delta\lambda_{eff}$	β_R(exp)	σ_P^E	($\sigma_P^E\times$ $\Delta\lambda_{eff}$)	($\sigma_P^E\times$ τ_R)	τ_{exp}	W_{NR}	η
SBT20L	$^4G_{5/2}\rightarrow^6H_{7/2}$	605	117.2	9.03	0.585	8.47	9.66	35.4	0.971	430	23.2
1.0LBTPE	$^5D_0\rightarrow^7F_2$	616	222.2	13.2	0.555	10.6	14.0	36.1	1.379	431	44.0
0.5LBTPS	$^4G_{5/2}\rightarrow^6H_{7/2}$	605	215.0	9.30	0.557	13.14	12.2	26.9	1.130	399	55.0
0.5LBTPD	$^4F_{9/2}\rightarrow^6H_{13/2}$	577	1556.2	6.52	0.616	111.6	72.8	46.2	0.345	423	85.0
TBZFE	$^5D_0\rightarrow^7F_2$	619	233.9	15.4	0.572	9.90	15.2	26.0	1.188	461	45.0

i) Salient features of the results on the effect of PbO on the B_2O_3–TeO_2–P_2O_5–BaO–CdO–Sm_2O_3 glasses

- Negative values of bonding parameter indicate predominant ionic nature of bonding between the Sm^{3+} ion and its ligands and the ionicity decreases with increasing the PbO content.
- The lower values of Ω_2 and Red/Orange ratio indicate the higher symmetry around the Sm^{3+} ion site.
- Decay curves of all the title glasses is of non-exponential behaviour. The measured lifetime of the $^4G_{5/2}$ energy level of the Sm^{3+} ions in the prepared glasses are found to increases with increasing the concentration of PbO content.
- The calculated colour coordinates, CCT and colour purity values of SBTXL glasses are found to lie in the reddish orange region of the CIE 1931 chromaticity diagram. These glasses are suitable candidates for the application in red lasers and display devices.
- Among the prepared glasses, SBT20L glass exhibits higher values of branching ratio (β_R), stimulated emission cross-section (σ_P^E), gain bandwidth product ($\sigma_P^E \times \Delta\lambda_{eff}$) and optical gain ($\sigma_P^E \times \tau_R$) values for the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition which indicate the prepared SBT20L glass is a potential candidate for the fabrication of photonic and optoelectronic devices.

ii) Salient features of the results on the red light generation through the lead boro–telluro–phosphate glasses activated by Eu^{3+} ions

- The bonding between the Eu^{3+} ion and the surroundings ligands are predominantly covalent nature.

- Direct and indirect band gap (E_g) values are found to decrease with increase the concentration of Eu^{3+} ions. This gradual decrease indicates that the formation of non-bridging oxygens in the glass network.
- High magnitude of Ω_2 and luminescent intensity ratio values indicate the lower symmetry and higher Eu-O covalence around the Eu^{3+} ions.
- Decay curves of all the XLBTPE glasses are found to be single exponential. This may be due to poor energy transfer in these glasses.
- Among the various transitions of XLBTPE glasses the $^5D_0 \rightarrow {}^7F_2$ transition possesses higher values of β_R, σ_P^E, $\sigma_P^E \times \Delta\lambda_{eff}$ and $\sigma_P^E \times \tau_R$ values for 1.0LBTPE glass. This suggests that the 1.0LBTPE glass is a suitable candidate to accomplish laser action and optical amplification.

iii) Salient features of the results on the structural and luminescence behaviour of Sm^{3+} ions doped lead boro–telluro–phosphate glasses

- Lower magnitude of Ω_2 and negative values of bonding parameter (δ) indicate higher symmetry around Sm^{3+} ions and dominant ionic nature of the bonding of Sm^{3+} ions with the surrounding ligands.
- The non-exponential decay curves (beyond the 0.5 wt % of Sm_2O_3) could be fitted to IH model with S = 6, indicating the dipole-dipole type of interaction between Sm^{3+} ions.
- x, y colour coordinates lie in the reddish orange region.
- Of the XLBTPS glasses, 0.5LBTPS glass possesses higher values of stimulated emission cross-section, optical gain and gain bandwidth product compared to the ones reported literature for other glasses.

- 0.5LBTPS glass is suitable for red laser applications.

iv) Salient features of the results on the structural and luminescence studies on Dy^{3+} doped lead boro–telluro–phosphate glasses

- Negative values of bonding parameter indicate the predominant ionic nature of the bonding of Dy^{3+} ion with the ligands of the glasses. Ionic nature increases with Dy^{3+} concentration.
- Direct and indirect band gap values increase with the increase of Dy^{3+} ion content. Higher Dy^{3+} ion content possess lower Urbach energy and it's suggested that minimum defects and less disorder in the title glasses.
- The JO parameters follow trend as $\Omega_2 > \Omega_4 > \Omega_6$ for all the XLBTPD glasses. The higher Ω_2 values of these glasses indicate the higher asymmetry around the Dy^{3+} ions.
- Decay curves exhibit single exponential behaviour at lower concentration and non-exponential nature at higher concentration.
- Decay curves match well with S = 6 (IH model) which confirms the fact that, the energy transfer between the Dy^{3+} ions is due to dipole-dipole interaction.
- Colour coordinates for all the glasses fall near to the ideal white light region.
- Among the prepared glasses, 0.5LBTPD glass possess higher Y/B ratios, A, σ_p^E, β_R, $\sigma_p^E \times \Delta\lambda_{eff}$, $\sigma_p^E \times \tau_R$ and η values for the $^6H_{13/2}$ emission transition suggesting its suitability for visible lasers and white LED applications.

v) Salient features of the results on the structural and luminescence studies of Eu^{3+}: TeO_2–B_2O_3–AO–AF_2 (A= Pb, Ba, Zn, Cd, Sr) glasses

- Positive values of bonding parameter, higher values of Ω_2 parameter and luminescent intensity ratio confirm the covalent nature of the bonding of Eu^{3+} ions with its surrounding ligands.
- Hypersensitive nature of the $^5D_0 \rightarrow ^7F_2$ transition confirms the higher covalency and asymmetry around the Eu–O bond and its ligands.
- Single exponential behaviour of the decay curve indicates negligible non-radiative energy transfer between the Eu^{3+}–Eu^{3+} ions.
- CIE colour coordinates and CCT values suggest that the TBXFE glasses are best suitable reddish orange light emitting diodes.
- Among the prepared glasses TBZFE glass exhibits higher laser parameters. This is a promising candidate for red laser applications at 616 nm.

Based on the obtained experimental results, it is suggested that SBT20L, 1.0LBTPE, 0.5LBTPS, 0.5LBTPD and TBZFE glasses are suitable candidates to design visible laser and optoelectronic devices for various optical applications.

8.3 Suggestions for further works:

- We have attempted to synthesis Sm^{3+}, Eu^{3+} and Dy^{3+}doped heavy metal borotellurite glasses. In future, studies may be extended to the other rare earth ions such as Tb^{3+}, Tm^{3+}, Nd^{3+}, Yb^{3+}, Ho^{3+} and Pr^{3+} in these glasses and glass ceramics for various visible lasers.
- Further investigations to improve the quantum efficiency, gain bandwidth product and optical gain of Sm^{3+}, Dy^{3+} and Eu^{3+} glasses with addition of appropriate co dopant prepared and studied.
- Optical absorption and luminescence studies may also be carried out at liquid helium / liquid nitrogen temperatures in order to elucidate good degree of information on the role of phonons in the relaxation process.
- The future work can be devoted to prepare glasses of larger dimensions in order to develop suitable photonic and optoelectronic devices.

List of journal publications

1. "Structural and Luminescence studies on Dy^{3+} doped lead boro−telluro−phosphate glasses"

   S. Selvi, G.Venkataiah, S. Arunkumar, G. Muralidharan, K. Marimuthu, Physica B, 454 (2014) 72−81.

2. "Structural and Luminescence behaviour of Sm^{3+} ions doped lead boro−telluro−phosphate glasses"

   S. Selvi, K. Marimuthu**,** G. Muralidharan, Journal of Luminescence, 159 (2015) 207−218.

3. "Red light generation through the lead boro−telluro−phosphate glasses activated by Eu^{3+} ions"

   S. Selvi, K. Marimuthu, N.Suriya Murthy, G. Muralidharan, Journal of Molecular Structure, 1119 (2016) 276−285.

4. "Effect of PbO on the B_2O_3−TeO_2−P_2O_5−BaO−CdO−Sm_2O_3 glasses − Structural and optical investigations"

   S. Selvi, K.Marimuthu, G.Muralidharan, Journal of Non-Crystalline Solids, 461 (2017) 35−46.

5. "Structural and luminescence studies of Eu^{3+}: TeO_2−H_3BO_3−AO−AF_2 (A= Pb, Ba, Zn, Cd, Sr) glasses"

   S. Selvi, K. Marimuthu, G. Muralidharan, Journal of Molecular Structure, DOI: 10.1016/j.molstruc.2017.05.031.

6.“Structural and Luminescence behavior of Eu^{+} ions doped lead boro–telluro–phosphate glasses”

S. Selvi, K. Marimuthu**,** G. Muralidharan, NCOPL conference Proceedings, ISBN No. 978–81–921895–0–6.

List of papers presented at conferences

1. “Structural and Luminescence behaviour of Sm^{3+} ions doped boro–tellurophosphate glasses”

   S. Selvi, G. Muralidharan, K. Marimuthu,

   National conference on luminescence and its applications (NCLA–2013) at PES Institute of Technology, Bangalore in 8-10 January 2013.

2. “Luminescence studies on Dy^{3+} doped lead boro–telluro–phophate glasses”

   S. Selvi, K. Marimuthu, G. Muralidharan,

   National conference on Luminescence and its Applications (NCLA–2014) held on February 4–6, 2014 at Rani Durgavathi University, Jabalpur.

3. “Structural and spectroscopic studies on Sm^{3+} doped lead boro–telluro–phophate glasses”

   S. Selvi, G. Muralidharan, K. Marimuthu,

   National conference on Advanced Materials (NCAM 2014) held on 24^{th} February, 2014 at St. Joseph College of Arts and Science, Tiruchirapalli.

4. “Spectroscopic investigations on Eu^{3+} doped Alkalifluoro Boro-Phosphate glasses”

V. Uma, S. Arunkumar, **S. Selvi**, K. Marimuthu,

National Conference on Advanced Materials (NCAM-2014) held at St. Joseph College of Arts and Science, Tiruchirappalli, Tamil Nadu on 24th February, 2014.

5. “Structural and luminescence behaviour on Eu^{3+} doped lead boro−telluro−phosphate glasses”

S. Selvi, K. Marimuthu, G. Muralidharan

National Conference on Optics, Photonics and lasers (NCOPL−14) held on 17th and 18th July 2014 at Arul Anandar College, Madurai.

6. “Optical studies of Eu^{3+}: TeO_2−ZnO−NH_6PO_4−NaF glasses”

S. Selvi, K. Marimuthu, G. Muralidharan

DAE-BRNS National Laser Symposium (NLS-23) on Dec 3−6, 2014, Venkateswara University, Thirupathi.

7. “Spectral analysis of Eu^{3+}: TeO_2 –H_3BO_3−AO−AF_2 (A= Pb, Ba, Zn) glasses”

S. Selvi, K. Marimuthu, G. Muralidharan

59th DAE – Solid state physics symposium to be held during Dec 16−20, 2014 at Vellore Institute of Technology, Vellore)

8. “Optical studies of Sm^{3+}: TeO_2−ZnO−NH_6PO_4−NaF glasses”

S. Selvi, K. Marimuthu, G. Muralidharan

5th International Conference on Luminescence and its applications (ICLA−2015), PES University, Bangalore, 9−12th February.

9. “Effect of PbO on the B_2O_3–TeO_2–P_2O_5–$BaCO_3$–CdO– Sm_2O_3 glasses for Red Laser applications”

S. Selvi, K. Marimuthu, G. Muralidharan

International conference on Sustainable energy technologies for smart and clean cities (SETS & CC-2016), Amara Raja Auditorium, Tirupati, 27–29th July.

10. “Europium doped zinc telluro-fluoro-phosphate glasses for red laser applications”

S. Selvi, K. Marimuthu, G. Muralidharan

International Conference on Renewable Energy and Environment (ICREE-2016), Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, 15–16th December 2016.

11. “Samarium doped zinc tellurofluorophosphate glasses: a strong candidate for red laser applications”

S. Selvi, P. Kathikeyan, K. Marimuthu, G.Muralidharan

DAE-BRNS National Laser Symposium (NLS-25), KIIT University, Bhubaneswar, Odisha, 20–23th December 2016.

12. “Effect of Dy^{3+} concentration on photoluminescence studies of zinc tellurofluoro phosphate glasses for WLED applications”

S. Selvi, K. Marimuthu, G. Muralidharan

National Conference on Recent Advances in the Applications Macromolecular Materials (RAAMM-2017), Gandhigram Rural Institute-Deemed University, Gandhigram, Dindigul, 2–3rd March 2017.