Effect of certain alkaline metals on Pr doped glasses to investigate spectroscopic studies.

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Abstract. Incorporation of different Alkaline earth metal like Barium, Calcium and strontium in sodium lead borate glass doped with Pr\textsuperscript{3+} is studied. Physical parameters such as density, molar volume, molar refractivity etc have been evaluated. Effect of different atomic size of alkaline metal using optical and physical parameters is analysed. XRD and FTIR were carried out to know the structural behaviour of the glasses. Absorption and Emission spectra are recorded at room temperature and the results were discussed.

1. Introduction

Currently for commercial applications Lanthanide dopant are extensively used to carry out research for variety of laser materials and optical components. Normally Borate glass former incorporated glasses have less refractive index, more melting point and phonon energies\cite{1,2}. After incorporation of heavy metal oxide like lead/bismuth/antimony into the borate matrix one can expect more changes regarding structurally and even changes in optical parameters are also observed \cite{3}. There is an assumption in previous literature that alkali and borate are to be used in equal proportion ratio \cite{4-8} whereas, later its reported that which is not mandatory to have alkali and borate in proportional ratio \cite{9}. Prasodymium doped glasses find variety of practical applications such as UV-VIS-NIR lasers, up-converters, optical fibre lasers and fibre amplifiers in 1.3 μm region \cite{10-13}. These applications can either be enhanced or optimized from systematic study of optical properties of Pr\textsuperscript{3+} ions in various environments.

In the present work we are reporting on Pr\textsuperscript{3+} ions doped optical behaviour of sodium lead barium/calcium/strontium glasses. The aim of the study is to know the effect of rare earth ion in certain alkaline borate glasses and also to observe the defects created when the Pr\textsuperscript{3+} ions are doped into it. Blue, green and red emission for visible region also infrared emission can be observed in Pr\textsuperscript{3+} ions doped glasses \cite{14}. We have studied the different alkaline earth metal ions effect on the Pr\textsuperscript{3+} doped glasses in detail to know the structural changes and optical studies of the present glass system.

2. Experimental

The samples of Pr\textsuperscript{3+} doped Alkaline (Barium, Calcium, Strontium) sodium lead borate glasses were synthesised by conventional melt quenching method. The composition details and naming is shown in table 1. The mixture of analytical grade sodium carbonate, lead oxide, Alkaline carbonates, boric acid and prasodymium trioxide (99.99\%) were mixed homogeneously in agate and motor for 30 minutes. The batch was melted in porcelain crucible at 1030-1050°C for 45 minutes (stirred for homogeneous mixing) and quickly poured on a preheated brass moulds to get pellet form samples which were polished for further analysis. Few physical parameters like density and refractive index were also calculated. The densities (ρ) of G series glasses samples were estimated using Archimede’s
relation in which toluene as submersion liquid. Refractive indices \( n \) of samples were measured at 589.3 nm (sodium wavelength) using an Abbe’s refractometer (Model CL: 1.30-1.71) with monobromonaphthalene as the contact liquid. The optical absorption spectra of polished samples have been recorded at room temperature in the wavelength range 400nm -800nm using Perkin Elmer lambda-35 UV-Vis spectrometer. The Photoluminescence spectrum has been recorded by Spectrofluorometer, Horiba Jobin Yvon Fluorolog-3,450W Xenon source with excitation 450nm.

| Table 1. Composition and naming of the glasses. |
|-----------------------------------------------|
| \( \text{Na}_2\text{O} \) | \( \text{PbO} \) | \( \text{Ba}_2\text{O}/\text{Ca}_2\text{O}/\text{Sr}_2\text{O} \) | \( \text{B}_2\text{O}_3 \) | \( \text{Pr}_2\text{O}_3 \) | \( \text{Naming} \) |
|---|---|---|---|---|---|
| 30 | 10 | - | 60 | - | G1 |
| 20 | 10 | 10 (\( \text{Ba}_2\text{O} \)) | 60 | 0.1 | G2 |
| 20 | 10 | 10 (\( \text{Ba}_2\text{O} \)) | 60 | 0.3 | G3 |
| 20 | 10 | 10 (\( \text{Ba}_2\text{O} \)) | 60 | 0.5 | G4 |
| 20 | 10 | 10 (\( \text{Ca}_2\text{O} \)) | 60 | - | G5 |
| 20 | 10 | 10 (\( \text{Ca}_2\text{O} \)) | 60 | 0.1 | G6 |
| 20 | 10 | 10 (\( \text{Ca}_2\text{O} \)) | 60 | 0.3 | G7 |
| 20 | 10 | 10 (\( \text{Ca}_2\text{O} \)) | 60 | 0.5 | G8 |
| 20 | 10 | 10 (\( \text{Sr}_2\text{O} \)) | 60 | - | G9 |
| 20 | 10 | 10 (\( \text{Sr}_2\text{O} \)) | 60 | 0.1 | G10 |
| 20 | 10 | 10 (\( \text{Sr}_2\text{O} \)) | 60 | 0.3 | G11 |
| 20 | 10 | 10 (\( \text{Sr}_2\text{O} \)) | 60 | 0.5 | G12 |
| 20 | 10 | 10 (\( \text{Sr}_2\text{O} \)) | 60 | - | G13 |

3. Results and discussion

3.1. Physical parameters:

Physical parameters are calculated for G1-G13 glasses and are reported in Table 2. The density \( \rho \) is measured using \( (W_a) \) weight of the glass sample in air, \( (W_b) \) weight of the sample when immersed in toluene of density \( \rho_x=0.8669 \text{gcm}^{-3} \),

\[
\rho = \frac{W_a}{(W_a-W_b)\rho_x}
\]  

...(1)

The determined volume \( V_m \) in molar is estimated using molecular weight (M.W) of the sample,

\[
V_m = \frac{M.W}{\rho}
\]  

...(2)

The molar refractivity \( (R_m) \) can be expressed in terms of refractive index and molar volume \( V_m \),

\[
R_m = \frac{n^2-1}{n^2+2} (V_m)
\]  

...(3)

The polarizabilities \( (\alpha_m) \) of these glasses can be calculated using the relation,

\[
\alpha_m = \frac{3}{4\pi N_A} R_m
\]  

...(4)

Where, molar refractivity \( (R_m) \) and Avogadro’s number \( (N_A) \).

The concentration of rare earth can be calculated by weight(x) of rare earth ion \( (\text{Pr}^{3+}) \), density \( \rho \) of the glass, Avogadro’s number\( (N_A) \), molecular weight(y) of Rare earth ion \( (\text{Pr}^{3+}) \).
The polaron radius \( (r_p) \) and inter ionic distance \( (r_i) \) can be calculated using the concentration of rare earth ion \( (N_i) \),

\[
r_p = \left( \frac{1}{2} \left( \frac{n}{6N_i} \right) \right)^{1/3}
\]
\[
r_i = \left( \frac{1}{N_i} \right)^{1/3}
\]

... (5)

Field strength \( (F) \) is now calculated by polaron radius, \( \frac{Z}{r_p} \),

\[
F = \left( \frac{Z}{r_p} \right)^2
\]

... (7)

Where, \( Z \) will be charge of rare earth ion. Dielectric constant \( (\varepsilon) \) will be square of refractive index and Reflection loss \( (R_L\%) \) of samples can be calculated using Refractive index, \( \left( \frac{n-1}{n+1} \right)^2 \),

\[
R_L = \left( \frac{n-1}{n+1} \right)^2
\]

... (8)

The refractive index of the present glass matrix is nearly 1.62 which is suitable for optical fibre applications[12]. The observed results of G1-G13 glasses shows that the density and molar volume are following the trend as expected, as the density decreases, the molar volume will increase. It’s also observed that due to the effect of different alkaline earth metals the density and molar volume is not similar in (G2-G5) barium incorporated glass, (G6-G9) calcium incorporated glass and (G10-G13) strontium incorporated glasses due to the different atomic size of barium, calcium and strontium[6,7]. In the present studies we can observe that molar volume is higher for barium incorporated glasses as shown in Fig.1, which may be due to the atomic size (G2-G5). In Fig.2 calcium and Fig.3 strontium incorporated glasses (G6-G13) molar volume and density compared to other samples (G2-G5) are less also as the concentration increases the inter-ionic distance decreases resulting in the increase in field strength of \( \text{Pr}^{3+} \) ion in the host matrix [8]. These variations are shown in Fig. 4.

| Glass | \( n \) | \( \rho (\text{g/cm}^3) \) | \( M.W \) (g) | \( V_m \) (cm³) | \( R_m \) (cm³) | \( \alpha_m \) \( (\times 10^{-24}) \text{cm}^3 \) | \( N_i \( (\times 10^{-20}) \text{ions/cm}^3 \) | \( r_p \) (nm) | \( r_i \) (nm) | \( F \) \( (\times 10^{-15}) \text{cm}^2 \) | \( R_L \% \) | \( \varepsilon \) |
|-------|------|----------------|---------|----------|---------|----------------|----------------|---------|---------|----------------|----------|-----|
| G1    | 1.627 | 3.092           | 82.685  | 26.74    | 9.477   | 3.752          | -                | -        | -        | -                | 5.697    | 2.647 |
| G2    | 1.624 | 2.975           | 91.817  | 30.86    | 10.894  | 4.314          | -                | -        | -        | -                | 5.655    | 2.637 |
| G3    | 1.625 | 3.756           | 92.147  | 24.53    | 8.670   | 3.433          | 0.489            | 1.776    | 2.776    | 0.951            | 5.669    | 2.640 |
| G4    | 1.622 | 3.561           | 92.807  | 26.06    | 9.174   | 3.632          | 1.386            | 1.256    | 1.962    | 1.901            | 5.627    | 2.630 |
| G5    | 1.62  | 3.441           | 93.466  | 27.16    | 9.538   | 3.777          | 2.216            | 1.074    | 1.680    | 2.60            | 5.687    | 2.624 |
| G6    | 1.624 | 3.36            | 82.498  | 24.55    | 8.666   | 3.431          | -                | -        | -        | -                | 5.656    | 2.637 |
| G7    | 1.629 | 3.06            | 82.425  | 26.93    | 9.563   | 3.786          | 0.446            | 1.832    | 2.862    | 0.893            | 5.717    | 2.652 |
| G8    | 1.626 | 3.404           | 83.085  | 24.40    | 8.634   | 3.419          | 1.470            | 1.231    | 1.924    | 1.979            | 5.682    | 2.643 |
| G9    | 1.627 | 3.308           | 83.744  | 25.31    | 8.970   | 3.552          | 2.367            | 1.051    | 1.642    | 2.719            | 5.697    | 2.647 |
| G10   | 1.626 | 3.686           | 86.849  | 23.56    | 8.337   | 3.301          | -                | -        | -        | -                | 5.682    | 2.643 |
| G11   | 1.628 | 3.365           | 87.179  | 25.90    | 9.183   | 3.636          | 0.464            | 1.808    | 2.825    | 0.919            | 5.703    | 2.648 |
| G12   | 1.627 | 3.393           | 87.839  | 25.88    | 9.172   | 3.632          | 1.387            | 1.256    | 1.961    | 1.901            | 5.696    | 2.647 |
| G13   | 1.623 | 3.38            | 88.498  | 26.18    | 9.231   | 3.655          | 2.296            | 1.061    | 1.658    | 2.664            | 5.641    | 2.634 |

Table 2. Physical parameters of G1-G13 glasses: Refractive index\((n)\), density \((\rho)\), Molecular weight\((M.W)\), molar volume \((V_m)\), molar refractivity \((R_m)\), polarizabilities \((\alpha_m)\), concentration of Rare earth ion \((N_i)\) , polaron radius \((r_p)\), inter ionic distance \((r_i)\), Field strength \((F)\), Reflection loss \((R_L\%)\) & Dielectric constant \((\varepsilon)\).
3.2. Structural properties

Amorphous nature of glasses was confirmed by XRD analysis which is shown in typical Fig.5. The broad hump confirms amorphous nature for the present G series glasses. The absence of peaks due to crystallization can be observed in the prepared glasses.

Fig.1. Density v/s molar volume of G2,G3,G4,G5 glasses.

Fig.2. Density v/s molar volume of G6,G7,G8,G9 glasses.

Fig.3. Density v/s molar volume of G10, G11, G12, G13 glasses.

Fig.4. Inter ionic distance v/s Field strength of glasses.
The vibration modes were analysed using FTIR spectra. Fig. 6 shows FTIR for all base glasses and Fig 7 shows barium incorporated base glasses with Pr\(^{3+}\) doped in it, Fig 8 shows calcium incorporated base glasses with Pr\(^{3+}\) doped in it and Fig 9 shows strontium incorporated base glasses with Pr\(^{3+}\) doped in it. FTIR spectra of present glasses from G1-G13 shows 5 prominent bands at ~600-770 cm\(^{-1}\), ~770-1180 cm\(^{-1}\), ~1180-1600 cm\(^{-1}\), ~2300 cm\(^{-1}\) ~2730 cm\(^{-1}\) and ~3465 cm\(^{-1}\). A weak band ~480 cm\(^{-1}\) is also observed. The band at ~600 cm\(^{-1}\) can be assigned to cage vibrations of metal ions such as Pb\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\) [10] and at ~600-770 cm\(^{-1}\) can be assigned due to bonding of B-O-B linkages (diborate linkage) [15-17]. Incorporation of lead oxide in borate glasses can result in creation of three and four coordinated boron’s which attributes to a Pb-O-B bending, resulting in [PbO\(_4\)]\(^{2-}\) or pyramidal units of metal ions overlaps with [BO\(_3\)] triangles [18]. The broad band ~770-1180 cm\(^{-1}\) can be assigned to B-O bond stretching of tetrahedral BO\(_4\) units from tri-, tetra- and penta- borate groups due to stretching vibration of B-O-M linkage (M represents metal ion). It may be due to vibrations of some boron atoms attached to non bridging oxygen in the form of BO\(_4\) vibrations [19,20]. Also we can expect stretching vibrations of B-O bonds in BO\(_4\) units from meta- and ortho- borate groups. B-O stretching vibrations of (BO\(_3\))\(^{3-}\) unit in meta borate and ortho- borate chains due to some B-O stretching of BO\(_4\) unit we may expect the shift in band due to asymmetric stretching vibrations of B-O bonds in BO\(_3\) units [21]. The bands at ~2300 cm\(^{-1}\), ~2730 cm\(^{-1}\) and ~3465 cm\(^{-1}\) can be assigned to Hydrogen bonding, molecular water and –OH bonding respectively [22].
3.3. Optical studies

The studies on absorption and emission spectra for the G1-G13 glasses to understand the optical behaviour of Alkaline Sodium Lead borate doped with Pr\(^{3+}\) ions is discussed in the following sub sections.

3.3.1. Absorption spectra

Spectra in visible region in the range 400nm -700nm range are recorded at room temperature for Pr\(^{3+}\) doped G series glasses. Fig 10 represents spectra of absorption for barium incorporated G2-G5 glasses which are doped with Pr\(^{3+}\) ions. Similarly Fig 11 represents absorption spectra of calcium incorporated G6-G9 glasses which are doped with Pr\(^{3+}\) ions also Fig 12 represents a spectra of absorption for strontium incorporated G10-G13 glasses which are doped with Pr\(^{3+}\) ions. We can clearly observe inhomogeneous prominent 4 peaks due to 4f transitions of Pr\(^{3+}\) ions. The 4 peaks at 442nm, 470nm, 480nm and 588nm are due to \(^3P\_2\), \(^3P\_1\), \(^3P\_0\) and \(^1D\_2\) respectively from \(^1H\_4\) ground state of Pr\(^{3+}\)ions [23]. The bands represents transition of Pr\(^{3+}\) doped alkaline incorporated G series glasses due to transits from ground state \(^1H\_4\) to \(^3P\_2\), \(^3P\_1\), \(^3P\_0\) and \(^1D\_2\). Since there is a effect of non homogeneoues broadening and stark splitting which are not resolved we can observe the transition are depicted in above said figures. G1, G2, G6 and G10 glasses are base glasses which doesn’t show any peaks in
UV-Vis region. Whereas others show, 4 peak with intensity variation due to the concentration variation of Pr\(^{3+}\) ions on the glasses. There is a change in intensity as the concentration of Pr\(^{3+}\) ions are increased. Among them, bands \(^3\)P\(_2\), \(^3\)P\(_1\), and \(^3\)P\(_0\) are overlapped and one independent peak at \(^1\)D\(_2\) is observed. In Fig. 10, for 0.5mol\% Pr\(^{3+}\), alkaline barium incorporation shows more intense peak for Pr\(^{3+}\) doped G5 glass compared to calcium and strontium G9 and G13 glasses as seen in Fig 11 and 12 respectively.

**Fig.10.** Absorption spectra of Barium incorporated glasses.

**Fig.11.** Absorption spectra of Calcium incorporated glasses.

**Fig.12.** Absorption spectra of Strontium incorporated glasses.

### 3.3.2. Emission spectra

Upon the excitation of 450nm the emission peaks are recorded in the visible region 450-750nm. Emission spectra in Fig 13, shows Pr\(^{3+}\) doped barium incorporated sodium lead borate glasses. Similarly in Fig 14 emission spectra represents Pr\(^{3+}\) doped calcium incorporated sodium lead borate glasses and Fig 15 shows emission spectra of Pr\(^{3+}\) doped Strontium incorporated sodium lead borate glasses. In all emission spectra we can observe 2 prominent band transitions at 494nm and 739nm which refers to \(^3\)P\(_0\)→\(^1\)H\(_4\) and \(^3\)P\(_0\)→\(^1\)F\(_4\) respectively [24]. Transition band at 603nm and 612nm is merged and overlapped refers to \(^3\)P\(_1\)→\(^1\)H\(_6\) and \(^3\)P\(_0\)→\(^1\)F\(_2\) respectively. Also very weak bands are seen at 526nm and 557nm for the transition \(^3\)P\(_1\)→\(^1\)H\(_5\) and \(^3\)P\(_0\)→\(^1\)H\(_5\) respectively [25].

Due to the incorporation of different alkaline metals such as barium, calcium and strontium emission peaks of G3-G5, G7-G9 and G11-G13 glasses varies. For 0.3mol\% Pr\(^{3+}\) doped glasses,
intensity is more in barium incorporated G3-G5 and strontium incorporated G11-G13 glasses. Where as in G7-G9 0.5 mol% Pr$^{3+}$ doped glasses is more intense. In G3-G5 and G11-G13 glasses after 0.3mol% Pr$^{3+}$ doping the intensity is decreased, this may be due to non–radiative transitions occurred in the glass matrix [26, 27]. This decrease in intensity can also be called as luminescence quenching. In our present glass (G3-G5, G7-G9 and G11-G13) can have two promising laser candidate as it is having emission in green and orange emitting transitions. Using the proper optimization method we can make use of these two lasers for photonic applications.

![Emission spectra of Barium incorporated glasses.](image1)

![Emission spectra of Calcium incorporated glasses.](image2)

![Emission spectra of Strontium incorporated glasses.](image3)

4. Conclusions

In the present investigation different alkaline metal incorporated into Pr$^{3+}$ doped G series glasses were studied. Glasses with the incorporation of varied atomic size exhibit nonlinear variation of density and volume. The physical parameter especially density values of Pr$^{3+}$ doped glasses are increasing as Pr$^{3+}$ concentration increased which infers that the present G series glasses are rigid in nature. Obtained glasses have nearly 1.62 refractive index with less reflection loss (<6%) are suitable for optical fibre glass. As observed $\mu$ is found decreasing as the Pr$^{3+}$ ion concentration increased for G series glasses which infers that atoms very tightly packed in our glass system. Present glasses G1-G13 consists more Borate unit’s vibration modes which is confirmed in FTIR analysis. Due to Pr$^{3+}$ions, $^3P_0$, $^3P_1$, $^3P_2$ and $^1D_2$ transition band is observed from $^1H_4$ ground state in G3-G5, G7-G9 and G11-G13 glasses. For the excitation of 450nm G3-G5, G7-G9 and G11-G13 glasses are exhibiting lasing
emission at 494 nm and 611 nm with an expectation that they can be used as multi lasing material. Further we can express that present glass systems are more stable for photonic applications.

5. References

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