

SPECTROSCOPIC INVESTIGATIONS OF Sm^{3+} & Dy^{3+} IONS DOPED ALKALI AND MIXED ALKALI BOROPHOSPHATE OXYFLUORIDE GLASSES

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Abstract : This article reports on the preparation and optical properties of Sm^{3+} , Dy^{3+} (0.25 mol %) ions doped glasses. The chemical composition of the glasses are given below:

64.75 B_2O_3 - 10 P_2O_5 - 10 ZnO -10 AlF_3 -5 (K_2CO_3 / Li_2CO_3 / Na_2CO_3) : 0.25 Sm^{3+} /0.25 Dy^{3+}

59.75 B_2O_3 - 10 P_2O_5 - 10 ZnO -10 AlF_3 -5 (Li_2CO_3 + Na_2CO_3 / Na_2CO_3 + K_2CO_3 / Li_2CO_3 + K_2CO_3): 0.25 Sm^{3+} /0.25 Dy^{3+}

FT-IR spectra of host glasses has been studied systematically and the functional groups are identified. The Vis-NIR absorption spectra of Sm^{3+} and Dy^{3+} glasses have been analyzed systematically. The emission spectrum of Sm^{3+} glasses exhibited three emission bands at 564nm, 600 nm and 647nm with an excitation wavelength of 404nm ($^6\text{H}_{5/2} \rightarrow ^4\text{I}_{9/2}$). Among them, the transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (600 nm) has shown a bright reddish-orange emission. In case of Dy^{3+} glasses two emission bands at 485 nm and 575 nm are observed with an excitation wavelength of 388 nm ($^6\text{H}_{15/2} \rightarrow ^4\text{K}_{17/2}$). Among these two, the transition $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ at 485 nm has shown a bright fluorescent blue emission.

IndexTerms - Sm^{3+} , Dy^{3+} : glasses, absorption, emission, excitation.

I. INTRODUCTION

Over the past several years, there has been a great deal of interest on the preparation and characterization of wide variety of optical glasses comprising oxides, silicates, borates, phosphates, and fluorides etc., for their potential applications [1-7]. Studies on the optical characterization of certain phosphate, and fluoride glasses have earlier been reported [8-14]. Mixing of oxide and fluoride ions in the preparation of glasses will combine the properties of both these ions i.e., oxyfluoride glasses will exhibit good thermal stability, moisture resistance and low multiphonon rates which have the value in between oxide and fluoride based glasses for a better emission efficiency [15-17]. Glass hosts with low phonon energy and stability are ideal for doping lanthanide ions as they reduce multi phonon relaxation, de excitation between lanthanide ions and favour in enhancing the quantum efficiency of luminescent transitions such materials find numerous applications in the field of photonic devices. Glasses based on phosphate, and fluorides have been identified as ideal optical systems because of their good glass forming ability, hardness, transparency, resistance towards the moisture without any degradation on their surfaces. In order to improve the glass quality and its optical performance from borophosphate oxyfluoride glasses, suitable quantity (5 mol%) of Li_2CO_3 , Na_2CO_3 , K_2CO_3 have been added as network modifiers (NMF) along with other properly improving network modifier AlF_3 . Rare-earth ions are incorporated into these glasses in order to characterize their behavior. For quite some time it has been known that rare-earth ions doped optical glassy materials have attracted a great deal of attention in different laboratories for a wide variety of potential applications in Optical amplifiers, sensors, LEDs and others [18-21]. Rare earth ions doped glasses have attracted a great deal of interest due to their important physical, chemical and optical properties. Recently, this class of glasses have been widely studied for their broad range of applications in of sensors, display monitors, optical data storage devices, optics communications and laser technology [22-25]. Rare-earth ions (RE^{3+}) would generally be existing in trivalent state, of which the $4f^n$ configuration could be found relatively isolated and the next excited $4f^{n-1}5d$ configuration lies in the high energy level above the ground state of the $4f^n$ configuration [26] and hence the electronic configuration causes the display of more sharp emission bands because of the intra f-f transitions. Among the rare earth ions, Sm^{3+} ($4f^5$) ion is one of the most interesting ion to analyze the luminescence properties as its emitting $^4\text{G}_{5/2}$ level exhibits relatively high quantum efficiency. Especially, glasses doped with Sm^{3+} ions were extensively investigated by optical spectroscopy to characterize these materials for optical device applications [27,28]. Similarly, Dy^{3+} ($4f^9$) ion is the best choice for investigating the dependence of its luminescent behaviour. The analysis of luminescence from $^4\text{F}_{9/2}$ level of Dy^{3+} ions is very interesting as it ranges in the visible and NIR regions. Optical properties of dysprosium doped glasses are attracting interest because of the 1.3 μm emission, which could be utilized for the optical amplification in telecommunication systems [29]. Also the intense yellow and bright blue emissions measured due to the transitions $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ from Dy^{3+} doped optical materials could be utilized in the development of solid state lasers in the visible wavelengths. Earlier we have reported on the optical analysis of Eu^{3+} , Tb^{3+} : B_2O_3 - P_2O_5 - ZnO - AlF_3 -(K_2CO_3 / Li_2CO_3 / Na_2CO_3) glasses [22]. In the present work, our main objective is to investigate the optical properties of newly developed 64.75 B_2O_3 - 10 P_2O_5 - 10 ZnO -10 AlF_3 -5 (K_2CO_3 / Li_2CO_3 / Na_2CO_3) : 0.25 Sm^{3+} /0.25 Dy^{3+} glasses and 59.75 B_2O_3 - 10 P_2O_5 - 10 ZnO -10 AlF_3 -5 (Li_2CO_3 + Na_2CO_3 / Na_2CO_3 + K_2CO_3 / Li_2CO_3 + K_2CO_3): 0.25 Sm^{3+} /0.25 Dy^{3+} glasses

II EXPERIMENTAL STUDIES

Four new series of 0.25 mol % of Sm^{3+} and Dy^{3+} ions doped in alkali and mixed alkali borophosphate oxyfluoride glasses were prepared in the following chemical compositions.

Series A:

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 -0.25 Sm_2O_3

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Na_2CO_3 -0.25 Sm_2O_3

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 K_2CO_3 -0.25 Sm_2O_3

Series B:

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 + 5 Na_2CO_3 -0.25 Sm_2O_3

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Na_2CO_3 +5 K_2CO_3 -0.25 Sm_2O_3

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 + 5 K_2CO_3 -0.25 Sm_2O_3

Series C:

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 -0.25 Dy_2O_3

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Na_2CO_3 -0.25 Dy_2O_3

64.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 K_2CO_3 -0.25 Dy_2O_3

Series D:

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 + 5 Na_2CO_3 -0.25 Dy_2O_3

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Na_2CO_3 +5 K_2CO_3 -0.25 Dy_2O_3

59.75 B_2O_3 -10 P_2O_5 -10 ZnO - 10 AlF_3 - 5 Li_2CO_3 + 5 K_2CO_3 -0.25 Dy_2O_3

The starting material in the present work were reagent grade of H_3BO_3 , $(\text{NaPO}_3)_6$, ZnO , AlF_3 , Li_2CO_3 , Na_2CO_3 , K_2CO_3 , Sm_2O_3 , and Dy_2O_3 . All chemicals were weighed appropriately in sensitive electronic balance, mixed thoroughly and powdered in a clean agate mortar. Each batch of freshly prepared powder weighing about 10 g was melt in clean and dry ceramic crucibles in an electrical muffle furnace for about one hour at constant temperature of 1000°C . These melts were quenched in between two brass plates to produce 2-3 cm diameter glass discs of 0.3 cm thickness each. The glasses thus obtained were annealed to 200°C for one hour to remove thermal strains if any. The prepared glasses were labelled as BPZALSm, BPZANSm, BPZAKSm for series A, BPZALNSm, BPZANKSm, BPZAKLSm for series B, BPZALDy, BPZANDy, BPZAKDy for series C and BPZALNDy, BPZANKDy, BPZAKLDy for series D. PLE and PL spectra were recorded using a Jobin Yvon Fluorolog - 3 fluoro-meter, with a Xenon flash lamp as an excitation source. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

3.1. Host glasses

The FT-IR spectra of host glasses are shown in Figs. 1&2. From the Figs. 1&2, it is observed that, IR bands related to BO_3 and BO_4 structural units of borate glasses

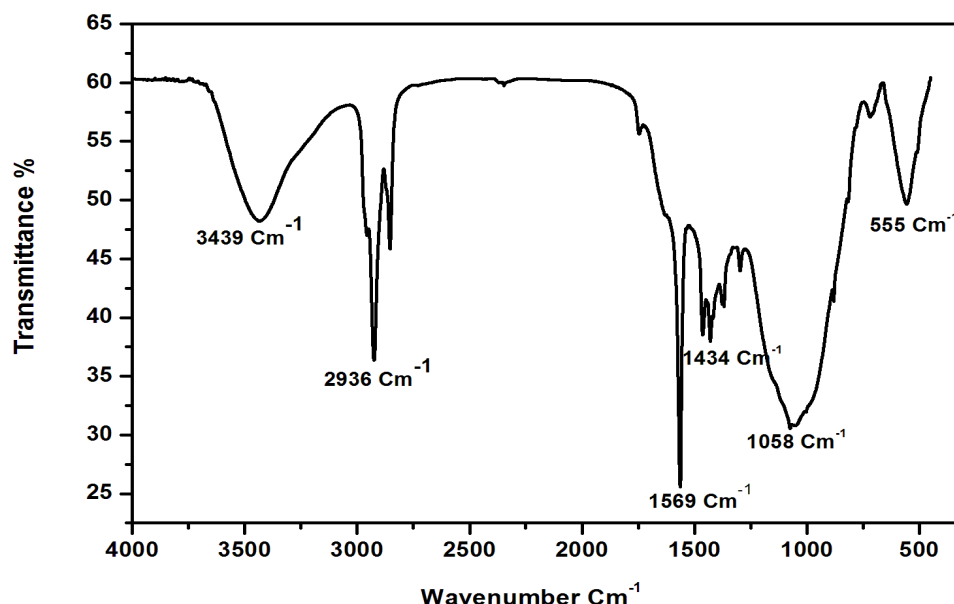


Fig.1: FTIR Spectrum of BPZALi (Series A) host glass

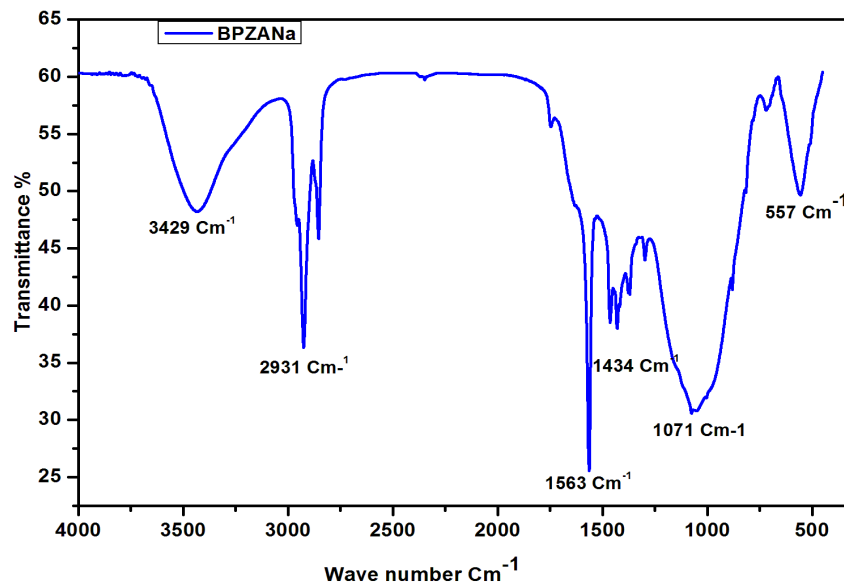


Fig.2: FTIR Spectrum of BPZALiNa (Series B) host glass

In the structure of borate glasses consists of a random network of BO_3 triangles with certain fraction of boroxol (six-membered) rings [11]. In the infrared spectral region, the vibrational modes of the borate network have three regions [12-14]. The $1000\text{--}1600\text{ cm}^{-1}$ band is the first region, which is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units. The second region is located between 500 and 1000 cm^{-1} due to the B-O bond stretching of tetrahedral BO_4 units and the last band around 700 cm^{-1} is because of the bending of B-O-B linkages in the borate network. Thus, the band around 1434 cm^{-1} arises from B-O stretching vibrations of $(\text{BO}_3)^{3-}$ unit in meta-borate chain and ortho-borates. The peak observed at 1058 cm^{-1} is attributed to the B-O bond stretching of BO_4 units. The absorption bands at 668 cm^{-1} and 761 cm^{-1} occurs from B-O-B bending vibrations. The absorption band around $500\text{--}600\text{ cm}^{-1}$ could be due to the deformational vibrations of PO_4 units with the changing compositions, which show little variations in positions in the range $500\text{--}600\text{ cm}^{-1}$ in both the glasses. In general, the IR absorption band at 806 cm^{-1} is assigned to a boroxal ring in the borate glass network. In the present study, the peak at 806 cm^{-1} is found missing, which indicates the absence of boroxal ring in the glass matrix. Similarly, the band in the region of $2900\text{--}3600\text{ cm}^{-1}$ is ascribed to the hydroxyl or water groups and the absorption band at 3439 cm^{-1} is attributed to symmetric OH stretching mode.

3.1. Sm^{3+} : glasses

Fig.3&4 shows the Vis-NIR absorption spectrum of Sm^{3+} : glass. The rare earth ions are characterized by partially filled $4f$ shell which is shielded by $5s^2$ and $5p^6$ electrons. All transitions in the absorption spectrum of Sm^{3+} start from the ground state $^6\text{H}_{5/2}$ to the various excited states. The transitions observed in the absorption spectrum of Sm^{3+} are intra configurational (f-f) transitions. The measured absorption spectrum has shown five absorption bands which are assigned to $^6\text{H}_{5/2} \rightarrow ^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, and $^6\text{F}_{3/2}$, transitions at 948 nm , 1080 nm , 1228 nm , 1371 nm , and 1477 nm respectively and the assignments have been made based on earlier reports [29,30].

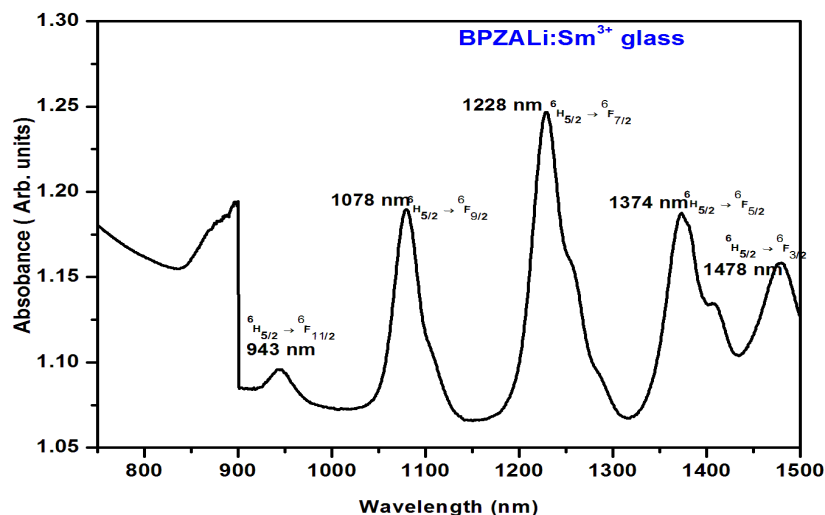


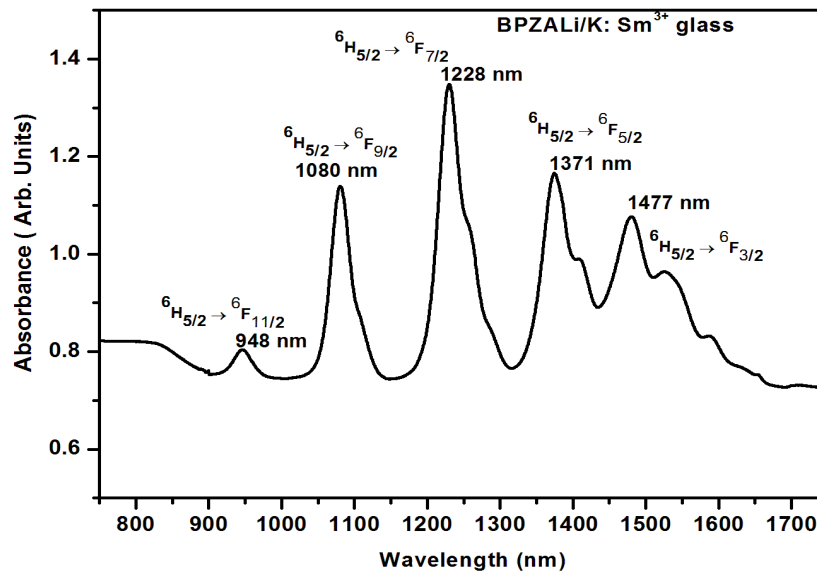
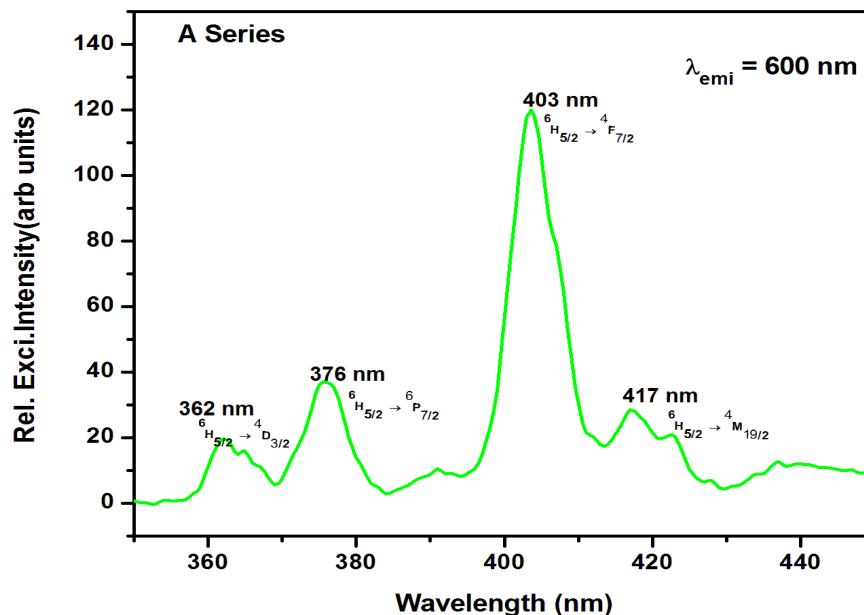
Fig.3: Vis-NIR absorption spectrum of (0.25 mol%) Sm^{3+} : BPZALi glassFig.4: Vis-NIR absorption spectrum of (0.25 mol%) Sm^{3+} : BPZALiK glass

Fig.5&6. shows the excitation spectrum of Sm^{3+} :glasses. The excitation spectrum has shown four excitation bands which are assigned to the electronic transitions $^6\text{H}_{5/2} \rightarrow ^4\text{D}_{3/2}$ at 360 nm, $^6\text{H}_{5/2} \rightarrow ^6\text{P}_{5/2}$ at 375 nm, $^6\text{H}_{5/2} \rightarrow ^4\text{F}_{7/2}$ at 404 nm, $^6\text{H}_{5/2} \rightarrow ^4\text{M}_{19/2}$ at 417 nm. Only the prominent excitation at 403 nm has been selected for the measurement of emission spectrum of Sm^{3+} glass. When the $^4\text{F}_{7/2}$ level (403 nm) of Sm^{3+} is excited, the initial population relaxes finally to the $^4\text{G}_{5/2}$ level. Between $^4\text{F}_{7/2}$ and $^4\text{G}_{5/2}$ levels, there are several levels with smaller energy differences, which encourage their efficient non radiative relaxation leading to the population of the $^4\text{G}_{5/2}$ state. This state is separated from the next lower lying $^6\text{F}_{11/2}$ by about 7000 cm^{-1} , which makes the multiphonon relaxation as negligible. Thus, it could be stated that radiative transitions and relaxation by non radiative energy transfer are the two main processes, which could finally depopulate the $^4\text{G}_{5/2}$ state.

Fig.5: Excitation spectrum of (0.25 mol%) Sm^{3+} : BPZALi glass

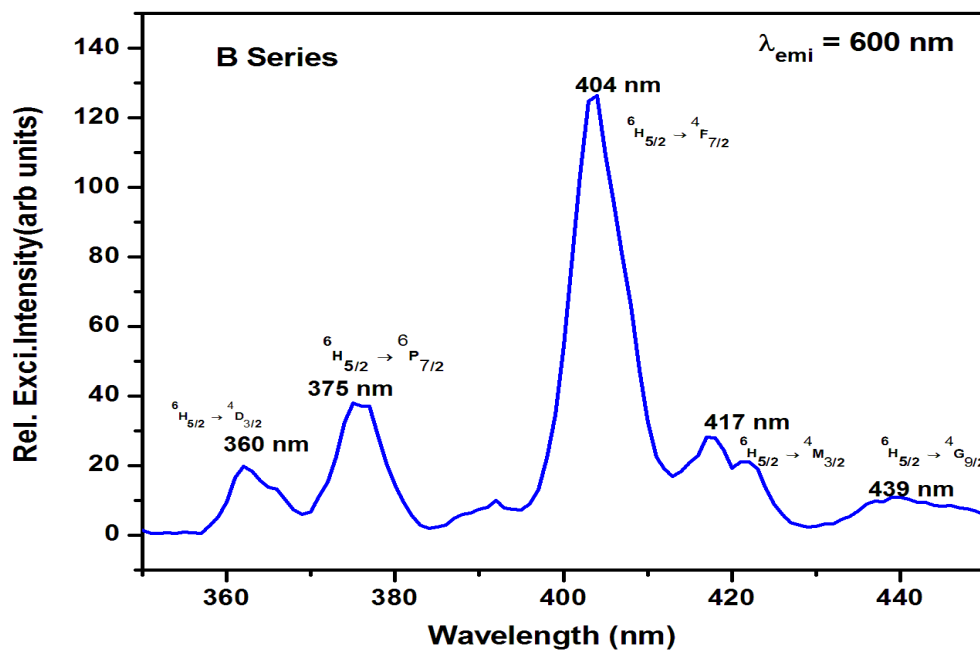


Fig.6: Excitation spectrum of (0.25 mol%) Sm^{3+} : BPZALi Na glass

The emission spectra of Sm^{3+} is shown in Fig.7&8, which has exhibited three emission transitions, which are assigned to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ (564 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (600 nm), $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ (647 nm) transitions. Among these three emissions bands, the transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ (600 nm), has shown strong emission. The Sm^{3+} : glass shows a bright orange-reddish emission under an UV source also. The transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ with $\Delta J = \pm 1$ is a magnetic dipole (MD) allowed but it is electric dipole (ED) dominated, the other transition $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ is purely an electric dipole one [31]. Generally, the intensity ratio of electric dipole to magnetic dipole transitions has been used to measure the symmetry of the local environment of the trivalent 4f ions. The greater intensity of the electric dipole transition; the more the asymmetry nature [32]. In the present work, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ electric dipole transition of Sm^{3+} ions is less intense than $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$ magnetic dipole specifying the asymmetric nature of the glass host. From the Figs.7&8, it is observed that, from series- A glasses, BPZALi: Sm^{3+} glass and from series- B glasses, BPZALiK: Sm^{3+} glass are having more luminescent intensity when compared to other glasses. Hence the more luminescence intensity glasses are potential candidates towards the novel optical device systems.

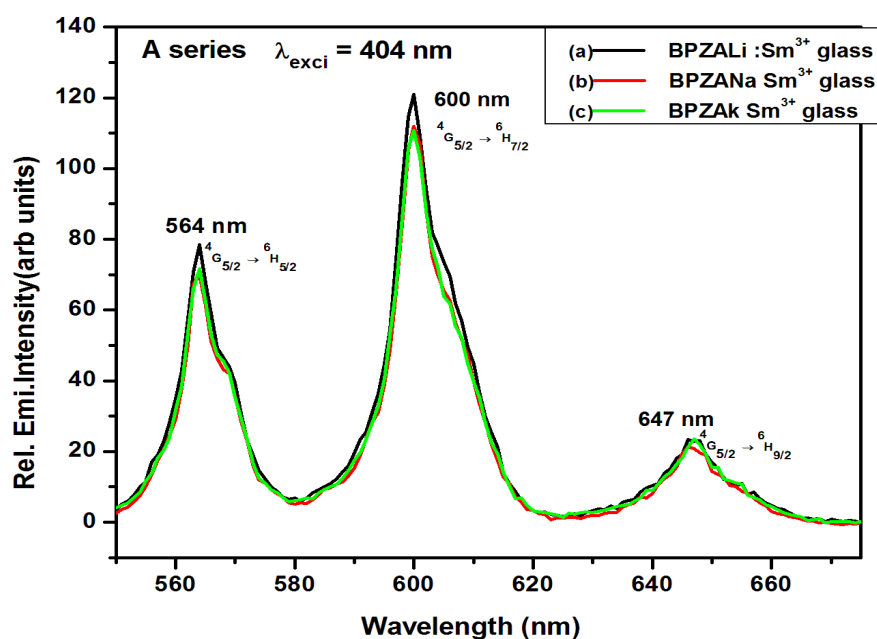


Fig.7: Emission spectra of (0.25 mol%) Sm^{3+} : glasses (Series A)

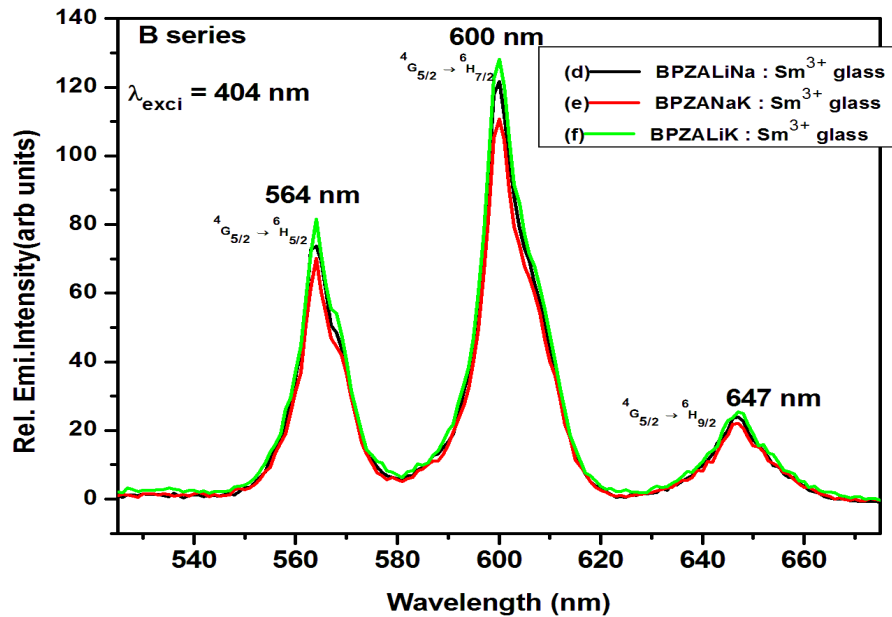


Fig.8: Emission spectra of (0.25 mol%) Sm^{3+} : glasses (Series B)

3.2 Dy^{3+} : glass

The VIS-NIR absorption spectrum of Dy^{3+} ion is shown in Fig.6. The bands are assigned from the ground state, $^6\text{H}_{15/2}$. The transitions from the next excited state $^6\text{H}_{13/2}$ may be ruled out due to thermalization as the energy gap between $^6\text{H}_{15/2}$ and $^6\text{H}_{13/2}$ is around 3000 cm^{-1} . From Fig.6 the levels of $^6\text{F}_{5/2}$, $^6\text{F}_{7/2}$, ($^6\text{H}_{7/2}$, $^6\text{F}_{9/2}$), ($^6\text{F}_{11/2}$, $^6\text{H}_{9/2}$) and $^6\text{H}_{11/2}$ are well resolved [21, 23]. The position and intensity of certain transitions of rare-earth ions are found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions [26]. All known hypersensitive transitions obey the selection rule $|\Delta S|=0$, $|\Delta L|\leq 2$, $|\Delta J|\leq 2$ [27]. In the case of Dy^{3+} ($4f^9$) ion, the hypersensitive transition ($^6\text{F}_{11/2}$, $^6\text{H}_{9/2}$) is found to be more intense than the other transitions.

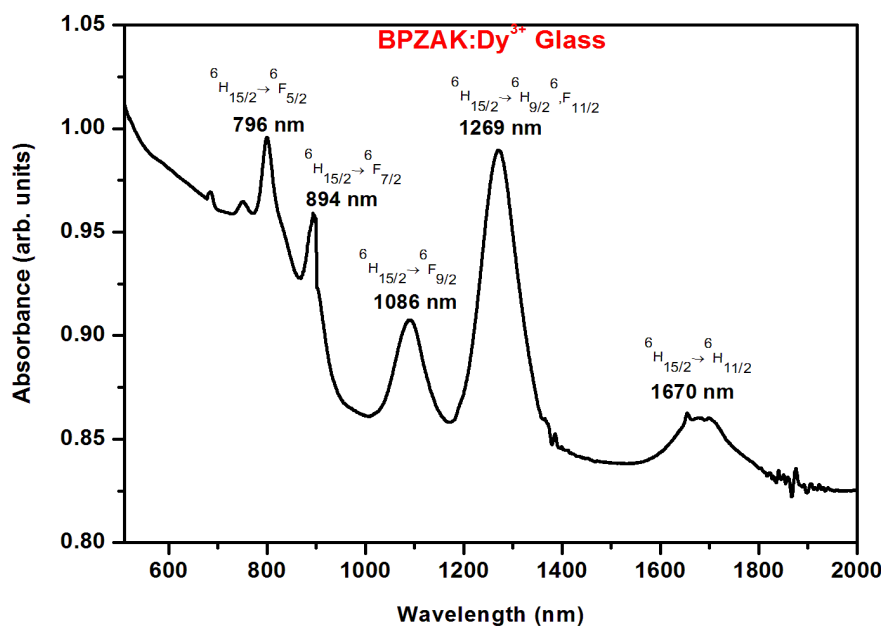


Fig.9: Vis-NIR absorption spectrum of (0.25 mol%) Dy^{3+} : BPZAK glass

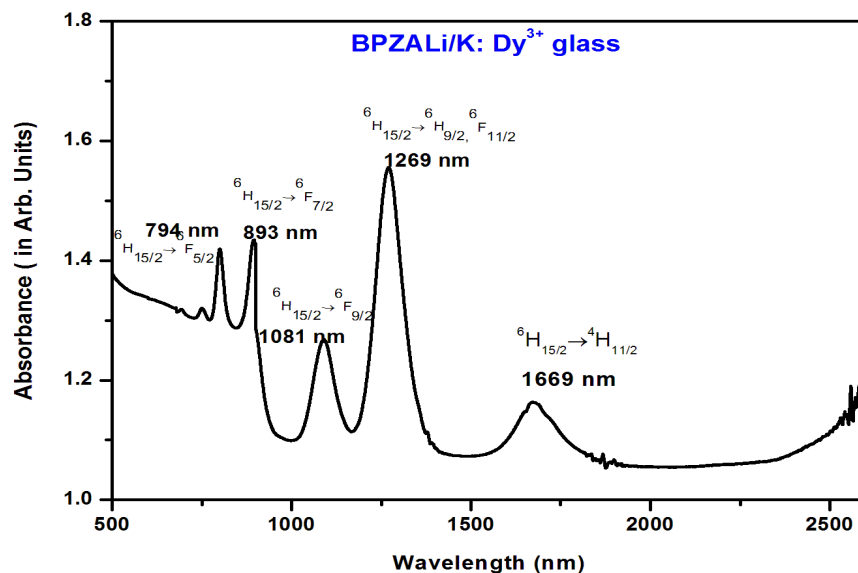


Fig.10: Vis-NIR absorption spectrum of (0.25 mol%) Dy^{3+} : BPZALiK glass

The excitation spectrum of Dy^{3+} : glass is shown in Fig.7, which was measured by monitoring intense emission at 483 nm. There are five obvious excitation peaks from the excitation spectrum, and these are assigned to the electronic transitions with the ground level $^6\text{H}_{15/2}$ to higher energy levels of Dy^{3+} , i.e. $^6\text{H}_{15/2} \rightarrow ^6\text{P}_{7/2}$ (350 nm), $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{13/2}$ (365 nm), $^6\text{H}_{15/2} \rightarrow (^4\text{I}_{13/2}, ^4\text{F}_{7/2})$ (388 nm), $^6\text{H}_{15/2} \rightarrow ^4\text{G}_{11/2}$ (426 nm) and $^6\text{H}_{15/2} \rightarrow ^4\text{I}_{15/2}$ (454 nm) based on the energy levels reported earlier [26,27]. From these excitation transitions, only a prominent transition (388 nm) has been selected for the measurement of emission spectrum of Dy^{3+} : glass. When the $^4\text{I}_{15/2}$ level of Dy^{3+} is excited with 451 nm wavelength, though this level is within thermal excitation energy at room temperature, we do not get any fluorescence from this level. The next eigen state of Dy^{3+} is $^4\text{F}_{9/2}$ whose energy from ground state is $\sim 20660 \text{ cm}^{-1}$. This state is separated from the next lower lying level ($^6\text{F}_{1/2}$) by about 6000 cm^{-1} , what makes the multiphonon relaxation negligible inspite of high phonon energies of the host ($\text{hw} \sim 1000 \text{ cm}^{-1}$). It appears that only radiative transitions and relaxation by non-radiative energy transfer processes could be depopulating the $^4\text{F}_{9/2}$ state [27]. From the Figs.7&8, it is observed that, from series- A glasses, BPZALi: Dy^{3+} glass and from series- B glasses, BPZALiK: Dy^{3+} glass are having more luminescent intensity when compared to other glasses. Hence the more luminescence intensity glasses are potential candidates towards the novel optical device systems.

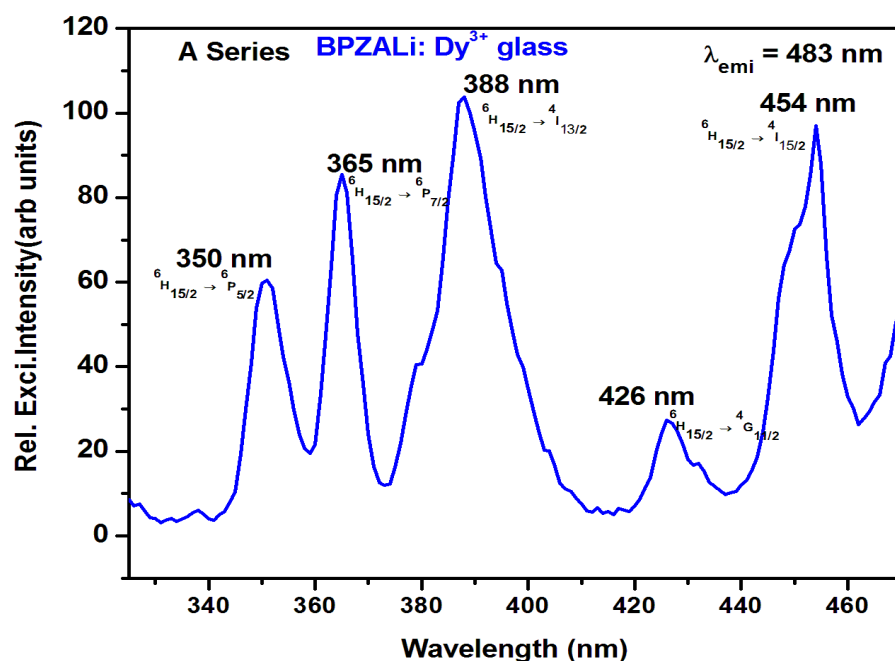


Fig.11: Excitation spectrum of (0.25 mol%) Dy^{3+} : BPZALi glass

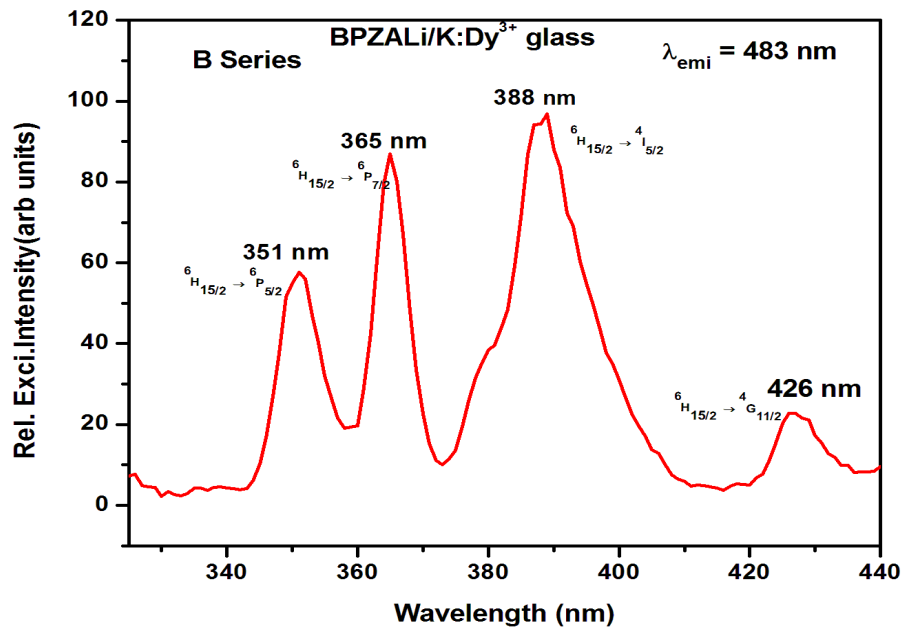


Fig.12: Excitation spectrum of (0.25 mol%) Dy^{3+} : BPZALi /K glass

The emission spectra of Dy^{3+} : glass is shown in Fig.13&14, which has shown two emission transitions, that are assigned to ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ (483 nm) and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ (575 nm) transitions. Among these transitions, the transition ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ has shown bright yellow emission intensity i.e. a major part of the emission intensity is contained in the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition.

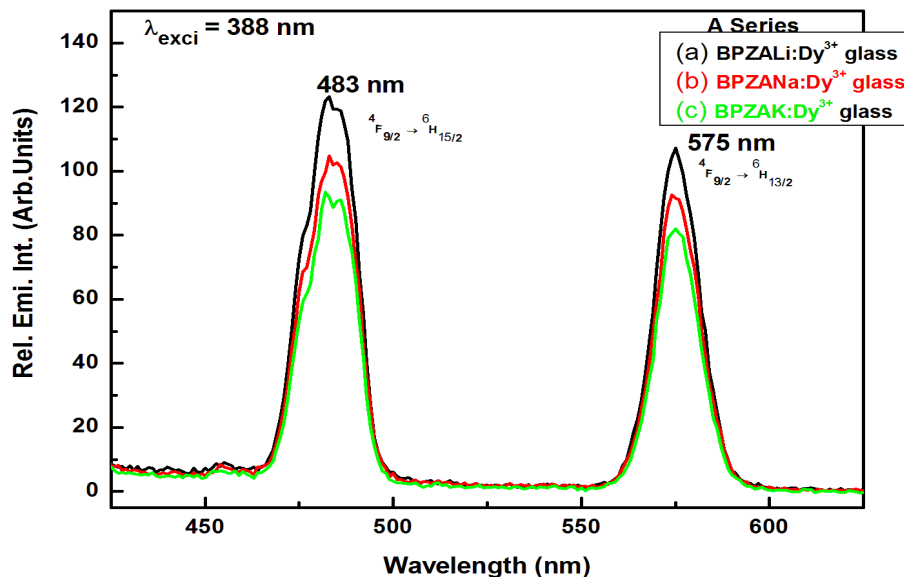


Fig.13: Emission spectra of (0.25 mol%) Dy^{3+} : glasses (Series A)

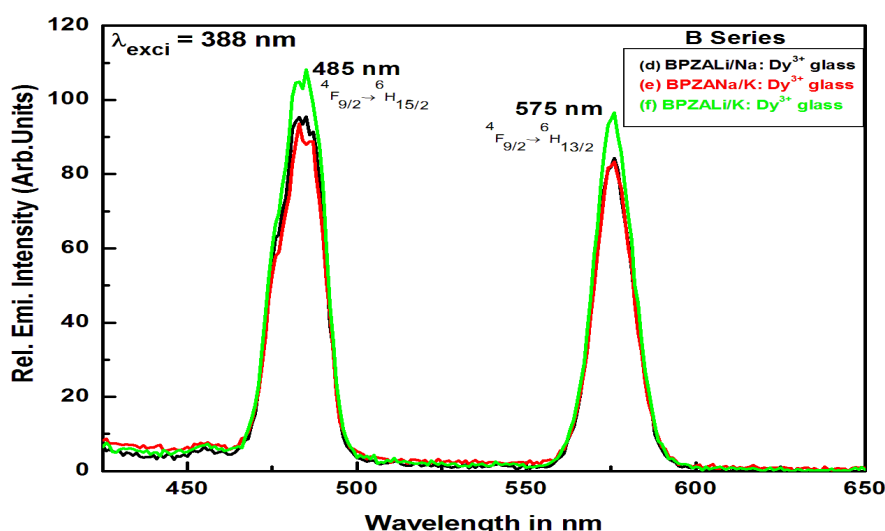


Fig.14: Emission spectra of (0.25 mol%) Dy^{3+} : glasses (Series B)

IV. CONCLUSION

In summary it is concluded that, (0.25 mol %) of Sm^{3+} and (0.25 mol %) Dy^{3+} : Sm^{3+} , Dy^{3+} : B_2O_3 - P_2O_5 - ZnO - AlF_3 -(K_2CO_3 / Li_2CO_3 / Na_2CO_3) glasses have been prepared by melt quenching method. From the FT-IR spectra, the functional groups are identified systematically. The Vis-NIR absorption spectra of Sm^{3+} and Dy^{3+} : glasses have been analyzed systematically. Samarium and dysprosium ions doped glasses have shown intense reddish-orange and yellow emissions respectively when placed under an UV source. Based on the spectral results, we suggested that Sm^{3+} and Dy^{3+} : glasses are highly potential enough towards display of luminescent materials of technological importance.

V. ACKNOWLEDGMENT

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