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Photoluminescence Spectrum of PbO-NaF-B_2O_3 Glass Doped with Ln^{3+} (Sm^{3+}/Ho^{3+}) Ions

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Abstract

Ln_2O_3 doped PbO-NaF-B_2O_3glasses were prepared and characterized through spectroscopic technique such as photoluminescence at room temperature to derive luminescence properties of Ln^{3+} ions in these glasses. Radiative properties which include radiative transition possibilities, branching ratios, radiative lifetime and stimulated emission cross sections of the fluorescent degree of Ln^{3+} ions in titled glasses are determined. In the present work all our systematic analysis has been presented with an example of results obtained in PbO-NaF-B_2O_3-Ln_2O_3 glasses. These results are used to access the gain media and in turn useful not only to write waveguides but also to modify the fluorescence properties through laser irradiation.

Keywords: Luminescence • B_2O_3, • Glasses • Radiative life time • Branching ratios

Highlights

Glasses from PbO-NaF-B_2O_3 doped with Sm_2O_3, Ho_2O_3 were prepared.
Ln3+ ions doped PbO-NaF-B_2O_3 glasses had their photo luminescence properties investigated.
Branching ratio, βr for the two glasses show the largest value for Glass 1(Sm^{3+} ions)

Introduction

Pure boron trioxide (B_2O_3) is covalently bonded, with particular structural features. The structural alternate between BO_3 and BO_4 outcomes the compactness of glass structure. It forms a random community with non-bridging oxygen, accommodating greater variety of RE ions. The choice of borate glass structures are because of its excellent ionic undertaking nature, low melting temperature, thermal balance and excessive transparency with rare earth do pant [1,2]. Oxides are appropriate substances for getting ready the green luminescence in rare earth ions [3]. Borate based glasses are exceptional for such luminescence host fabric purpose, which clearly shows the variations in its structural residences with alkaline earth cations [4].

Ln^{3+} ions doped glasses have found great interest for fiber amplifiers, up conversion lasers and display devices. To identify new optical devices with specific utility, with enhanced performance active research is being to carry out by selecting the hosts doped with Ln^{3+} ions.

A large number of studies especially on optical properties of various rare earth ions doped glasses and crystals are available in the literature [5-12]. For the present study one of the rare earth ions viz., Ln^{3+} has been chosen for the doping in PbO-NaF-B_2O_3 glass matrix with a read to possess an inspiration over the attainable use of those glasses as optical device hosts. For this purpose fluorescence properties of these glasses have been investigated. It is well known that the optical characterization of the glasses, i.e., the study of glass transparency and their ability to accept rare earth ions as the luminescent centers is essential for their use in glass optical device technology. Alkali fluoroborate glasses particularly are tremendous as laser hosts in view in their optical transparency over a wide range of wavelength.

Sm^{3+} ions doped laser substances are of interest in lasers for subsequent technology nuclear fusion. These materials can be used as a gain media in the microchip laser at high doping levels, since this rare earth ion has a very simple energy level scheme with desirable properties for a laser system [13]. In the emission spectra of Sm^{3+} ion, the transitions, $^4G_{5/2}\rightarrow{}^6F_{9/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ occurring in the near infrared and visible region respectively are also identified as hypersensitive [14].

Ho^{3+} ion have the electronic configuration, $4f^{10}$ with $5I_8$ ground state [15]. It gives a large number of well resolved absorption and emission transitions in the ultraviolet, visible and near infrared region. Many of the emission transitions of Ho^{3+} are lasing transitions in crystals but only one laser transition has been identified in glass hostes, viz., $5I_7\rightarrow 5I_8$ [16].

Further while those glasses are combined with specific community enhancing ions, we may also assume the structural adjustments and local field variations around Sm^{3+} ions and Ho^{3+} ions; such modifications may also have strong referring to numerous luminescence transitions in PbO-NaF-B_2O_3 glasses. Composition of 10PbO-19 NaF-70B_2O_3-1.0 Ln_2O_3 is chosen and a systematic investigation of photoluminescence has been carried out.

Materials and Methods

Composition of the glass

From the approximate glass forming region for the present ternary PbO-

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NaF-B_2O_3 system seems we have chosen following composition for Ln^{3+} ions doping. The detailed chemical composition of the glass samples and their codes are presented in Table 1.

Table 1. Composition of glass samples (all in mol %)

Sample code	PbO	NaF	B_2O_3	Ln_2O_3
Glass 1	10	19	70	1.0 Sm_2O_3
Glass 2	10	19	70	1.0 HO_2O_3

Methods of preparation of glasses

The glasses used for the present study are prepared by the melting and quenching techniques [17-19]. The starting materials used for the preparation of the present glasses were Analytical grade reagents of H_3BO_3, NaF, PbO and Ln_2O_3, The glasses were melted in the temperature range 1100°C for a 1 hour till a bubble free liquid was formed. The approximate final dimensions of the glasses used for studying photoluminescence properties are 1 cm × 1 cm × 0.2 cm. Schematic representation of preparation of glass samples are shown in Figure 1.

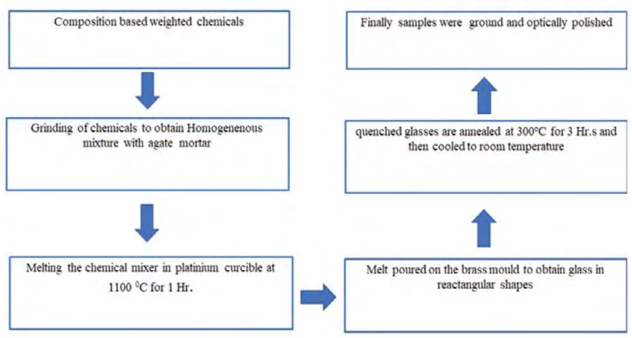

Figure 1. Schematic representation of preparation of glass samples

Spectroscopic properties

The photoluminescence spectra of glasses were recorded on Photon Technology International fluorescence spectrophotometer in UV and NIR regions with a monochrometer and photomultiplier tube for detecting the luminescence response in the appropriate wavelength regions.

Results and Discussion

The room temperature fluorescence spectra of Sm^{3+}: PbO-NaF-B_2O_3 glasses excited at 400 nm has exhibited the following transitions (Figure 2)

$$^4G_{5/2} \rightarrow {}^6H_{5/2}, {}^6H_{7/2}, {}^6H_{9/2.}$$

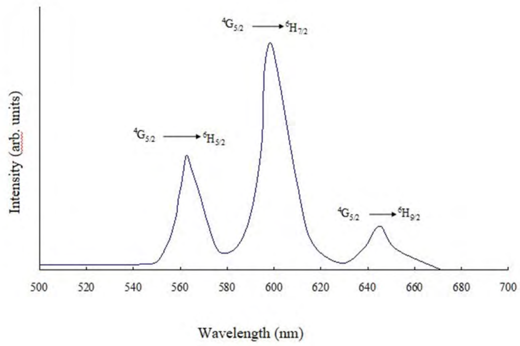

Figure 2. Photoluminescence spectrum of Sm3+ doped PbO-NaF-B2O3 glasses (λexc=400 nm) recorded at room temperature. All the transitions are from the upper state 4G5/2.

The radiative properties viz., the spontaneous emission probability A, the total emission probability A_T involving all the intermediate terms, the radiative life time (τR) and the fluorescent branching ratio βr and the stimulated emission cross section σ_P^E of various fluorescence levels observed for the present glasses are determined and presented in Table 2.

Table 2. Data on radiative properties of Sm_{3+}: PbO-NaF-B_2O_3 glasses

Emission Transition	λ (nm)	δλ (nm)	A (S^{-1})	A_T (S-1)	Br%	Emission cross section (σ_P^E) X 10^{-21} (cm^{-2})
$^4G_{5/2} \rightarrow {}^6H_{9/2}$	630	10.4	3085	46360.8	65.59	0.02
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	581	11.8	4194	46360.8	9.04	0.21
$^4G_{5/2} \rightarrow {}^6H_{7/2}$	549	15.1	1089	46360.8	2.32	3.62
Life time τR)=20.49μs						

The measured wavelength λ of the peak, half width Δλ and the computed value of the stimulated emission cross section σ^E_P for two prominent emission transitions viz., $^4G_{5/2} \rightarrow {}^6H_{5/2}, {}^6H_{7/2}, {}^6H_{9/2}$ are also presented in Table 2 for Sm^{3+} ions doped glasses.

Do The room temperature fluorescence spectra of Ho^{3+}: PbO-NaF-B_2O_3 glasses excited at 395 nm has (Figure 3), exhibited the following transitions and the stimulated emission cross section σ^E_P of various fluorescence levels observed for the present glasses are determined the values are presented in Table 3.

$$^4F_3 \rightarrow {}^5I_{8,}\ {}^4G_5 \rightarrow {}^5I_{7,}\ {}^5I_6, {}^5I_{5,} \text{and } {}^5S_2 \rightarrow {}^5I_{8.}$$

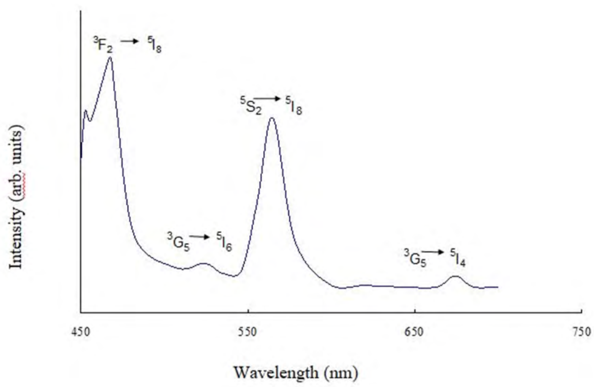

Figure 3. Luminescence transitions from 5I8 state of Ho3+ ions in PbO-NaF-B2O3 glasses (λexc=395.3 nm) recorded at room temperature

Table 2. Data on radiative properties of Ho_{3+}: PbO-NaF-B_2O_3 glasses

Emission Transition	λ (nm)	δλ (nm)	A (S^{-1})	A_T (S-1)	Br%	Emission cross section (σ_P^E) X 10^{-21} (cm^{-2})
$^4F_2 \rightarrow {}^5I_8$	470	19	1896	6251	30.19	0.74
$^5S_2 \rightarrow {}^5I_8$	552	20	1070	2633	40.68	0.61
Life time τR)=0.152μs						

The luminescence spectra of Ln^{3+} ions are similar to those reported for a number of other glass systems [20-24]. The high intensity or high quantum yield of the luminescence bands of Ln^{3+} ion in the glasses indicates that there is a minor cross relaxation, i.e., the shift of energy from the excited state of Sm-ion by electric multipole interaction to neighboring Sm-ion lying in the ground state is low for this particular glass when compared with other glass.

The radiative properties of Ln^{3+} ions depend on the number of factors such as network former and modifier of the glass. The value of βr of the luminescence transitions characterizes the lasing ability of the laser transitions. The βr values obtained for the luminescent transitions originated from $^4G_{5/2}$ level for all the two glasses have been furnished in Tables 2 and 3.

Referring to the data on emission transitions, the transition $^4G_{5/2} \rightarrow {}^6H_{9/2}$, has the highest value of βr for all the two glasses; this transition may therefore be considered as a possible laser transition. However, the comparison of βr values of this transition for the two glasses show the largest value for glass 1 indicating these glasses to exhibit better lasing.

Conclusion

Photoluminescence of Ln^{3+}: PbO-NaF-B_2O_3 glass structures were studied. The radiative transition probabilities and branching ratios evaluated for numerous luminescent transitions are determined in the luminescence spectra. The photoluminescence spectra recorded at room temperature for those glasses have exhibited the bands similar to the subsequent transitions:

$$Sm^{3+} \text{ glasses: } {}^4G_{5/2} \rightarrow {}^6H_{5/2},\ {}^6H_{7/2},\ {}^6H_{9/2}$$

$$Ho^{3+} \text{ glasses: } {}^5F_3 \rightarrow {}^5I_8,\ {}^5G_5 \rightarrow {}^5I_7,\ {}^5I_6,\ {}^5I_5 \text{ and } {}^5S_2 \rightarrow {}^5I_8$$

The comparison of the values the branching ratio, βr for the two glasses show the largest value for Glass 1(Sm^{3+} ions) indicating these glasses to exhibit better lasing action.

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