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Optical Absorption Spectra of PbO-NaF-B_2O_3 Glass doped with Ln^{3+} (Sm^{3+}/ Ho^{3+}) Ions

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ABSTRACT

Optical properties like, optical absorption studies are measured for Ln^{3+}ions doped PbO-NaF-B_2O_3glasses. Standard samples of PbO-NaF-B_2O_3glass system were prepared by the melt quenching technique. From the optical absorption PbO-NaF-B_2O_3glass the Judd-Oflet theory could successfully be applied to characterize the optical absorption spectra of these ions for all the glass systems. Out of the three J-O parameters (Ω_λ), the value of Ω_2 which is related to the structural changes in the vicinity of the Ln^{3+} ion indicated gradual changes in the covalent environment.

Keywords: Optical absorption, B_2O_3,glasses, J-O parameters

I. INTRODUCTION

A number of studies on optical properties of various rare earth ions doped glasses are available in the literature [1-4]. 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 view to have an idea over the possible use of these glasses as laser hosts. For this purpose optical absorption properties of these glasses have been investigated. During the last few years large varieties of new inorganic glasses have been developed and characterized [5-7]. Alkali fluoroborate glasses specially are wonderful as laser hosts in view in their optical transparency over a huge variety of wavelength. In addition, those glasses posses a completely decrease charge of crystallization, excessive transparency and proof against moisture. It is therefore felt worthwhile to investigate their optical properties after incorporating a rare earth ion, Ln^{3+} in them.

Samarium ion exists in Sm^{3+} and Sm^{2+} states however among those states; Sm^{3+} is discovered to be greater stable. This ion has $^4f_5$ electronic configuration with $^6H_{5/2}$ ground state. Earlier it was shown that the oscillator strengths of Sm^{3+} ions may be arranged in two groups, one referring to transitions up to 10,700 cm^{-1} and the second to transitions in the range 17,600-32,800 cm^{-1} and the Judd-Ofelt parameters can be calculated separately for these two regions [8]. The transitions $^6H_{5/2} \rightarrow {}^4F_{3/2}$, $^4F_{3/2}$ of Sm^{3+} occurring in the absorption spectrum in the near infrared region is hypersensitive [9, 10].Optical characterization of Sm^{3+} doped borate glasses are identified as a better laser host material [11].

Ho^{3+} ion have the electronic configuration, $4f^{10}$ with $^5I_8$ ground state [12]. It gives a large number of well resolved absorption and emission transitions in the ultraviolet, visible and near infrared region. The two transitions of Ho^{3+} in the absorption spectra viz., $^5I_8 \rightarrow {}^5G_6$ and $^5I_8 \rightarrow {}^5H_6$ are hypersensitive [13-16]. The former is governed by the quadrupole selection rules ($\Delta S = 0$, $\Delta L.\Delta J \leq 2$). Weak visible fluorescence of Ho^{3+} has been observed in phosphate glasses from $^5S_2$, $^5F_4$ and $^5F_5$ levels to the terminal $^5I_8$ level. Optical transitions of Ho^{3+} in fluorozirconate glasses have been well characterised and lasing has been observed for the transition $^5I_7 \rightarrow {}^5I_8$ in this glass .

II. Composition of the Glass

From the approximate glass forming region for the present ternary PbO-NaF-B_2O_3 system seems we have chosen following composition for Ln^{3+} doping.

The details of the glasses used for the present studies are:

Glass 1: 10 PbO-19NaF-70B_2O_3- 1.0 Sm_2O_3

Glass 2: 10 PbO-19NaF-70B_2O_3- 1.0 Ho_2O_3

III. 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 900°C for a 1 hour till a bubble free liquid was formed. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1 cm x 1 cm x 0.2 cm.

Optical Properties

Under the optical properties: the optical absorption of PbO-NaF-B_2O_3 glasses doped with rare earth oxides was studied. The optical spectra of PbO-NaF-B_2O_3 glasses doped with Ln_2O_3 were recorded using a Shimadzu-3101 UV–VIS-NIR Spectrophotometer in the wavelength range 350-900 nm. From the absorption spectrum, the observed bands are assigned to the appropriate transitions.

IV. Results

The optical absorption spectrum of Sm^{3+} doped PbO-NaF-B_2O_3 glasses recorded at room temperature in the wavelength region 300-2500 nm has exhibited absorption bands, all from the ground state $^6H_{5/2}$. (Fig. 1) gives the absorption spectra of these glasses; these levels are assigned to the following appropriate electronic transition [20]:

$^6H_{5/2} \rightarrow {}^4I_{11/2}, {}^4I_{13/2}, {}^4G_{9/2}, {}^6P_{5/2}, {}^4F_{7/2}, {}^6P_{7/2}, {}^4D_{5/2}, {}^4K_{17/2}$

The spectral intensities for the prominent observed bands of these glasses have been analysed with the help of Judd-Ofelt theory. Judd – Ofelt intensity parameters Ω_λ for these glasses were evaluated and these parameters are presented in Table 1.

The optical absorption spectrum of Ho^{3+} doped PbO-NaF-B_2O_3 glasses recorded at room temperature in the wavelength region 300-2500 nm has exhibited seven absorption bands, all from the ground state $^5I_8$. Fig. 2 gives the absorption spectrum of Glass 2; these levels are assigned to the following appropriate electronic transition:

$^5I_8 \rightarrow {}^5G_5, {}^5G_6, {}^5F_2, {}^5F_3, {}^5F_4, {}^5F_5, {}^5I_6, {}^5I_7$

The spectral intensities for the prominent observed bands of these glasses which can be expressed in terms of oscillator strength of forced electronic dipole transitions have been analysed with the help of Judd-Ofelt theory. Judd – Ofelt intensity parameters Ω_λ for these glasses were evaluated and these parameters are presented in Table 2

The bonding parameter, (δ), [21, 22] has also been computed for all the glasses presented in Table 3. Among the two alkaline earth oxide modifier glasses, the highest values of δ obtained for Glass 1 indicate the highest covalent environment of Sm^{3+} in this glass.

The J–O parameters have been observed to be in the following order for all the glasses $\Omega_2 > \Omega_4 > \Omega_6$. The collection of the data on Ω_λ parameters of Ln^{3+} ion in various glass matrices is shown in Table 3 along with the comparison of the parameters for each glass host.

V. Discussion

The energies and spectral profiles of certain transitions in the absorption spectra of Ln^{3+} ions throw some light on their co-ordination [23-25]. Ω_λ values for Ln^{3+} ions in the glasses systems in general give information about the environment of the rare earth ions in the glass lattice. The rare earth ions in the glass systems are randomly distributed over non equivalent sites with distribution in the crystal fields; this was proved by simulation studies and a number of optical studies [26, 27] .

These ions which occupy sites with non-centro symmetric potential contribute significantly to Ω_2 [28]. For the crystalline systems it is generally expected the higher values for Ω_2 than those of free ions. Such discrepancies may arise due to the influences of the dielectric of media, the covalence [29, 30].

Normally, the parameter Ω_2 is associated with the covalence and / or structural modifications in the vicinity of the Ln^{3+} ion (short-range effect) and Ω_4 are related to the long-range effects. The larger modifier ion (Ba^{2+} ionic radius, 1.34 Å) in glasses give rise to a large average distance between the B-O-B chains which results in the average Ho-O distance to increase, therefore producing a weaker field around the Ho^{3+} ion leading to a low value of Ω_2 when compared with that of other glasses. Further aid for this argument also can be noted from the fee of the bonding parameter δ; the value of δ for these glasses follows the order Glass 1 (Sm_2O_3) > Glass 2 (Ho_2O_3) indicating the high covalent environment for Sm^{3+} ions in Glass 1 and high ionic environment in Glass 2.

The recorded optical absorption spectral profiles of Ln^{3+}ions doped PbO-NaF-B_2O_3 glasses have revealed the following transitions:

$^6H_{5/2} \rightarrow {}^4I_{11/2}, {}^4I_{13/2}, {}^4G_{9/2}, {}^6P_{5/2}, {}^4F_{7/2}, {}^6P_{7/2}, {}^4D_{5/2}, {}^4K_{17/2}$ (Sm^{3+})

$^5I_8 \rightarrow {}^5G_5, {}^5G_6, {}^5F_2, {}^5F_3, {}^5F_4, {}^5F_5, {}^5I_6, {}^5I_7$ (Ho^{3+})

By performing least square fitting analysis the J-O parameters for these glasses are computed and are found to show the following trend for all glasses.

The value of δ (bonding parameter), gives information on the covalent environment of Ln^{3+} ions in the glass matrix. The larger the value of δ, the larger is the covalent environment of Ln^{3+} ions in the glass matrix. Among the Four glasses doped with Ln^{3+} ions, the highest values of δ obtained for Glass 1 indicate the highest covalent environment of Sm^{3+}.

VI. Conclusions

The optical absorption PbO-NaF-B_2O_3 glass system with variable concentrations of Ln^{3+} has been studied. The Judd-Ofelt theory could successfully be applied to characterize the optical absorption spectra of these ions for all the glass systems. Out of the three J-O parameters (Ω_λ), the value of Ω_2 , which is related to the structural changes in the vicinity of the Ln^{3+} ion indicated gradual changes in the covalent environment as the concentration of Ln_2O_3 is varied.

Information about the covalent environment of Ln^{3+} ions in the glass matrix can be identified by δ. The larger the value of δ, the larger is the covalent environment of Ln^{3+} ions in the glass matrix. Among the glasses doped with Ln^{3+} ions, the highest values of δ obtained for Glass 1 indicate the highest covalent environment of Sm^{3+}. The obtained results indicate that optical properties of Ln^{3+} doped PbO-NaF-B_2O_3 glasses has yielded some valuable information which may be helpful for using these glasses for practical applications.

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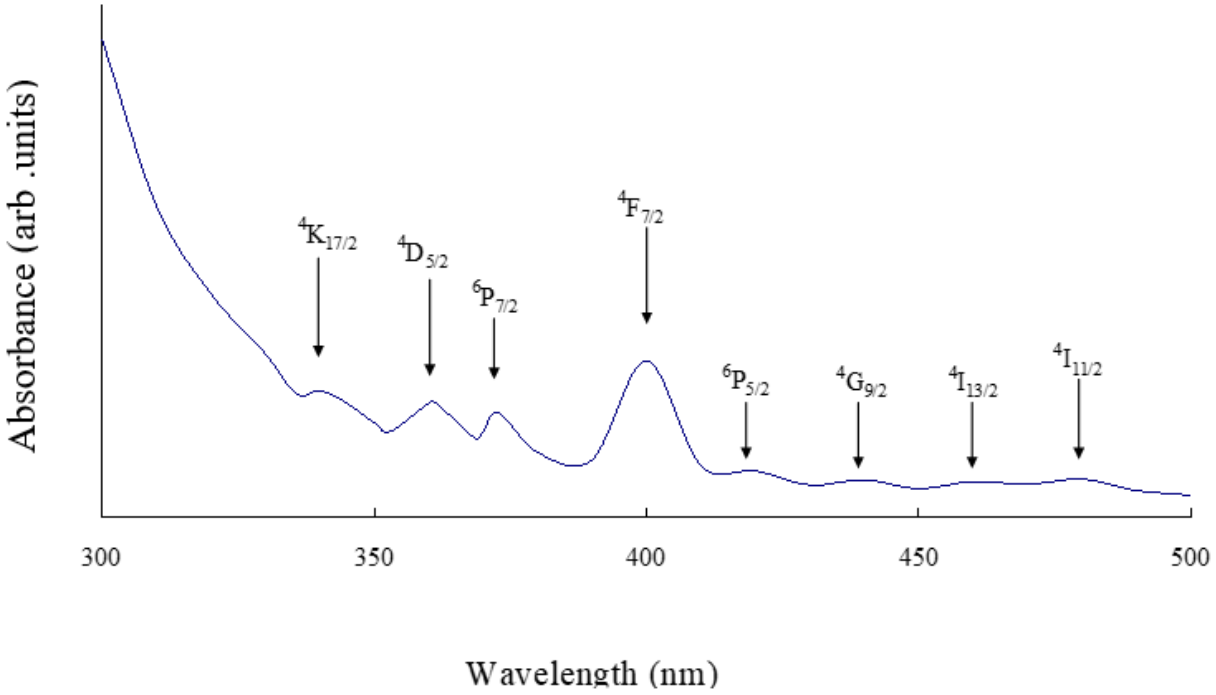

Fig.1. Optical absorption spectrum PbO-NaF-B_2O_3 glasses doped with Sm^{3+} ions recorded at room temperature. All the transitions are from the ground state $^6H_{5/2}$

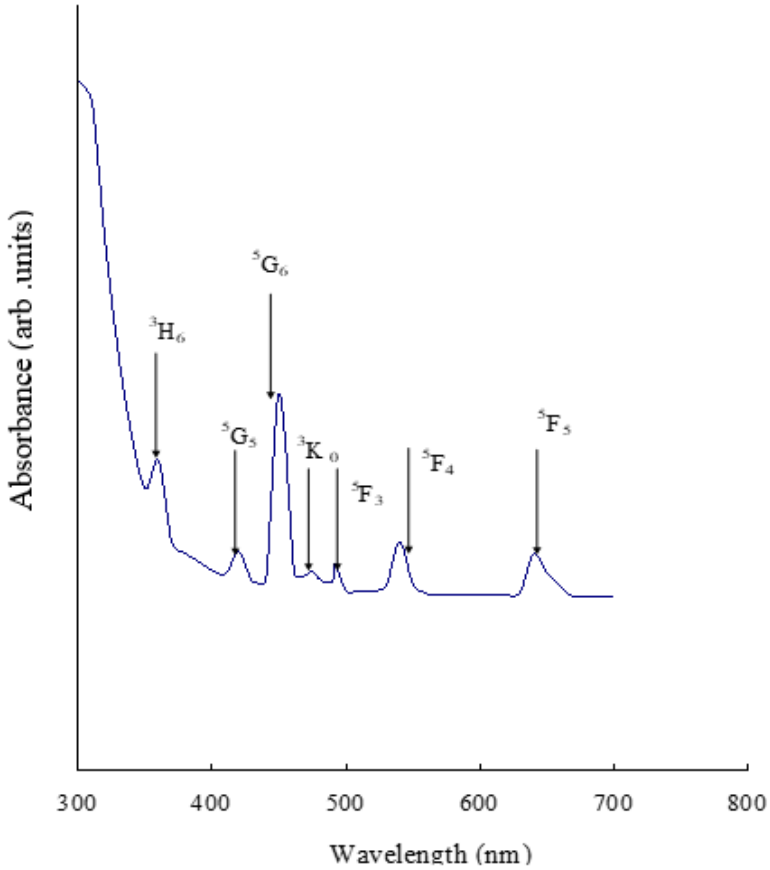

Fig.2. Optical absorption spectrum PbO-NaF-B_2O_3 glasses doped with Ho^{3+} ions recorded at room temperature. All the transitions are from the ground state $^5I_8$

Table 1

The absorption band energies and the oscillator strength (*f*) for some transitions of Sm^{3+}: PbO-NaF-B_2O_3glasses (**Glass 1)**

Transition	Energy $(cm)^{-1}$	f_{exp} x 10^{-6}	f_{theo} x 10^{-6}
$^6H_{5/2}\rightarrow{}^4I_{11/2}$	20790	1.23	1.07
$^6H_{5/2}\rightarrow{}^4I_{13/2}$	21264	1.02	1.42
$^6H_{5/2}\rightarrow{}^4G_{9/2}$	22513	2.33	5.61
$^6H_{5/2}\rightarrow{}^6P_{5/2}$	23809	2.51	4.17
$^6H_{5/2}\rightarrow{}^4F_{7/2}$	24992	1.79	1.13
$^6H_{5/2}\rightarrow{}^6P_{7/2}$	26216	0.96	0.61
$^6H_{5/2}\rightarrow{}^4D_{5/2}$	27356	9.8	9.30
$^6H_{5/2}\rightarrow{}^4K_{17/2}$	29148	4.6	6.51

Table 2

The absorption band energies and the oscillator strength (*f*) for some transitions of Ho^{3+}: PbO-NaF-B_2O_3glasses (**Glass 2)**

Transition	Energy $(cm)^{-1}$	f_{exp} x 10^{-6}	f_{theo} x 10^{-6}
$^5I_8\rightarrow{}^5G_5$	23870	0.17	0.13
$^5I_8\rightarrow{}^5G_6$	22065	4.6	4.7
$^5I_8\rightarrow{}^5F_2$	21008	0.71	0.87
$^5I_8\rightarrow{}^5F_3$	20564	0.39	0.59
$^5I_8\rightarrow{}^5F_4$	18720	0.26	0.26
$^5I_8\rightarrow{}^5F_5$	15671	0.17	0.18

Table 3

J-O parameters of Ln^{3+} doped PbO-NaF-B_2O_3 glasses

Glass	Ω_2 (x10^{-20}) (cm^2)	Ω_4 (x10^{-20}) (cm^2)	Ω_6 (x10^{-20}) (cm^2)	(Ω_4 / Ω_6)	Bonding parameter δ
Glass 1	25.6	4.3	1.4	3.071	-0.02
Glass 2	5.17	2.7	5.5	0.490	-0.05