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Spectroscopic Investigations on Pr^{3+} Doped Alkali Fluoroborophosphate Glasses

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ABSTRACT

Alkali fluoroborophosphate glasses doped with praseodymium fluoride has been prepared and characterized by X-Ray diffraction, UV–Visible spectroscopy, differential scanning calorimetry, excited and emission spectra analysis. Judd-Ofelt theory has been applied to evaluate the optical parameters such as radiative transition probabilities, radiative lifetime, branching ratios etc. of praseodymium, Pr^{3+}, ions. The trend found in the JO intensity parameter is $\Omega_6 > \Omega_4 > \Omega_2$, it indicates the glass system is favorable for the lasing emission $^1D_2 \rightarrow {}^3H_4$ in IR wavelength. Among the studied glasses, the glass with 20 mole% of NaF appears to be an ideal material for carrying out further investigations on samples of appropriate size to examine laser action to use them in glass laser technology and optical communications.

1. Introduction

Optically potential ions such as trivalent rare earth (RE^{3+}) doped glasses have been investigated extensively because of their applications in various fields such as luminescent systems, solid state lasers, fiber amplifiers, flat panel displays, planar waveguides and optical data storage etc., [1-5]. In trivalent rare earth (RE^{3+}) ions, Praseodymium based glasses are of special interest because of their peculiar physical properties such as low melting point, high dielectric constant, high refractive index and high chemical durability [6]. Among trivalent rare earth ions, Pr^{3+} is a good optical activator, which offers the possibility of simultaneous blue, green and red emissions for laser action as well as IR emission for optical amplification [7] and these special properties can either be enhanced or optimized from systematic study of Pr^{3+} ions in various environments [8, 9].

Fluoride based glasses are well adapted for many of technological applications and with a content of borophosphate is another attractive candidate as a ultra-violet transmitting material [10, 11]. Fluoroborophosphate glasses possess high mechanical strength when compared with pure borate glasses [6]. In this paper, author report the important results from the physical, absorption and luminescence properties of Pr^{3+} doped glasses with alkali fluorides [LiF, NaF and KF] as network modifiers.

2. Experimental Methods

2.1 Synthesis of AFBP Glasses

Pr^{3+} doped alkali fluoroborophosphate (AFBP) glass samples $30(NaPO_3)_6{:}20B_2O_3{:}10BaF_2{:}10ZnF_2{:}8AlF_3{:}20xF{:}2PrF_3$ (where x = Li, Na and K) have been prepared by melt-quenching method and are presented in Table 1. Analytical reagent grade chemical used in the present study were thoroughly mixed by using an agate pestle mortar and subjected to melt in a porcelain crucible at 1050 °C by an electrical muffle furnace for 2 hours. After complete melting, the melts were quickly poured in to a brass disc and subsequently and annealed at temperature of 300 °C for 2 h to remove thermal strains and stresses. The glass samples so prepared were of good optical quality and were transparent, circular in shape with 2-3 cm in diameter and uniform thickness of 0.2 cm.

Table 1 Composition of Glasses (mol%)

Glass	$(NaPO_3)_6$	B_2O_3	BaF_2	ZnF_2	AlF_3	LiF	NaF	KaF	PrF_3
AFBP1	30	20	10	10	8	20			2
AFBP2	30	20	10	10	8		20		2
AFBP3	30	20	10	10	8			20	2

2.2 Characterization Techniques

X-ray diffractions of the powder samples at room temperature were obtained using Philips X-ray generator (Model PW1170) with CuKα radiation (λ=1.5418 Å) in 2θ ranges from 10° to 70° with a step size of 2° per minute. The differential scanning calorimetry (DSC) measurements were performed using Netzsch DSC 204 instrument. A small amount of material about 5 mg was taken in the aluminum pan of the DSC setup and scanned at a heating rate of 10 °C/min. Optical absorption spectra of these glasses were recorded at room temperature in spectral wavelength range covering from 200-900 nm using Hitachi model U2000 UV-Vis-NIR spectrophotometer. Both the excited and emission spectra of these glasses have been recorded on a Hitachi F3010 Spectrofluorometer.

3. Results and Discussion

3.1 X-Ray Diffraction

Fig. 1 represents the XRD pattern of the sample (AFBP1) which shows the absence of Bragg's peak, but only a broad diffuse hump around low angle region. This is the understandable indication of amorphous nature within the resolution limit of XRD instrument.

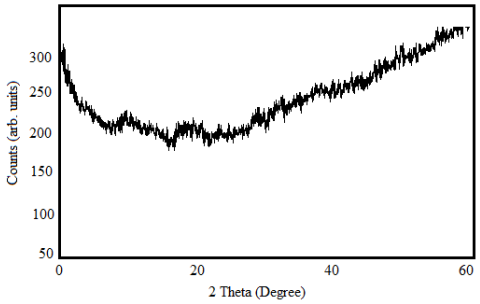

Fig. 1 XRD spectrum of Pr^{3+} doped alkali fluoroborophosphate glass (AFBP3)

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3.2 Physical Properties

Assortments of physical properties of present glasses are evaluated using conventional formulae [12-14] and measured the values of refractive index, average molecular weight and density. These physical properties are presented in Table 2. Among all the physical properties of glasses density is one of the effectual parameter to investigate the grade of structural compactness. The molar volume and density of the glass network depend upon many factors such as structure, cross-link density, dimensionality of interstitial spaces and coordination number [15, 16]. In the present work it is observed that the successive replacement of alkali content the average molecular weight increases from AFBP1 glass to AFBP3 glass, which influences density and other physical properties. The variations in physical properties of a glass are found to be very sensitive to the ionic size and atomic weight [17]. Difference in properties also infers that environment around Pr^{3+} ions are different in different glasses which are due to replacement of alkali fluoride effects.

3.3 DSC Thermogram Studies

DSC thermogram of AFBP3 glass is shown in Fig. 2. The glass exhibited an endothermic change due to the glass transition temperature (T_g) occurred at 610 °C. For higher temperatures the sampled glass exhibited an exothermic change due to crystallization temperature (T_c) reported at 695 °C. The value of T_c - T_g is 85 °C, this value present the information on the stability of the glass against devitrification.

Table 2 Physical properties of Pr^{3+} doped alkali fluoroborophosphate glasses

Physical property	Glass		
	AFBP1	AFBP2	AFBP3
Refractive index (n_d) at 589.3 nm	1.516	1.514	1.520
Density d (g/cm³)	1.496	1.497	1.499
Average molecular weight $\overline{M}$ (g)	239.45	242.66	245.88
Pr^{3+}ion concentration N (x10^{22} ions/cm³)	75.26	74.31	73.39
Mean Atomic Volume (g/cm³/atom)	14.04	14.22	14.40
Optical Dielectric constant	1.298	1.292	1.295
Dielectric constant (ε)	2.298	2.292	2.295
Reflection losses (R)(%)	4.206	4.180	4.193
Molar Refraction R_m(cm^{-3})	48.34	48.80	49.50
Polaron radius r_p(Å)	1.600	1.621	1.641
Interionic distance r_i(Å)	5.057	5.079	5.100
Molecular Electronic polarisability α (x10^{-23} cm³)	0.958	0.967	0.981
Field strength F (x10^{15}cm^{-2})	11.72	11.42	11.14
Optical basicity (Λ_{th})	0.5736	0.5763	0.5799

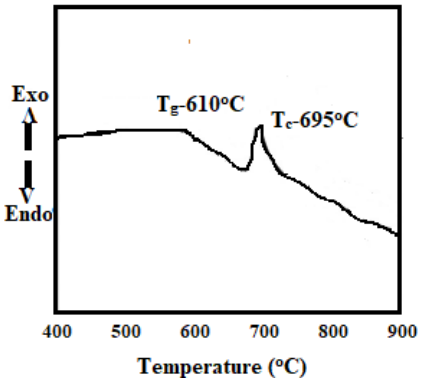

Fig. 2 DSC traces of Pr^{3+} doped alkali fluoroborophosphate glass (AFBP3)

3.4 Optical Absorption Studies

The absorption spectra of Pr^{3+} doped AFBP glass specimens have been represented in Figs. 3 and 4. The spectra consists of eight absorption bands in UV-VIS and NIR region corresponding the ground state $^3H_4$ to excited states $^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^3F_4$, $^3F_3$, $^3F_2$ and $^3H_6$ of Pr^{3+} ions. The optical absorption bands around the $^3P_2$ (448 nm), $^3P_1$ (470 nm), $^3P_0$ (480 nm), $^1D_2$ (590 nm), $^3F_4$ (1420 nm), $^3F_3$ (1537 nm), $^3F_2$ (1933 nm) and $^3H_6$ (2370 nm) are assigned from the ground state, $^3H_4$ [18]. The micro symmetry around Pr^{3+} ions differ slightly from site to site. As a result, the transitions are in homogeneously broadened with typical half widths of about 100 cm^{-1} for isolated bands. Overall the appearance of the spectra is very similar and only very minuscule changes in the spectral peak positions of the absorption bands and relative intensities by the replacement of alkali fluorides one with other in glass matrix are observed. In additional Judd-Ofelt (J-O) intensity parameters Ω_λ (λ = 2, 4 and 6) were calculated by conventional J-O theory [19, 20] and evaluated values are presented in Table 3. In the present study the three Ω_λ parameters follow the trend $\Omega_2 < \Omega_6 < \Omega_4$. The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 1.39 and 3.05 in the present glasses. Among the three J-O parameters evaluated for Pr^{3+} ions in these three glasses, the Ω_2 parameter involves the most significant term of the crystal field potential and is vastly responsive to local structural changes [21-23]. In the present case of study the value of Ω_2 parameter increases from glass to glass with successive replacement of alkali fluoride content. This is due to increasing alkali size and ionic radii from Li to K.

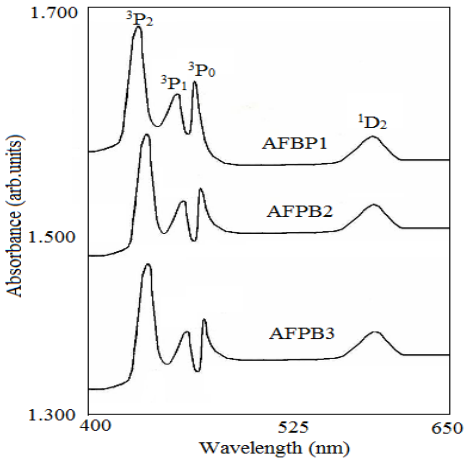

Fig. 3 Optical absorption spectra of Pr^{3+} doped alkali fluoroborophosphate glasses in visible region

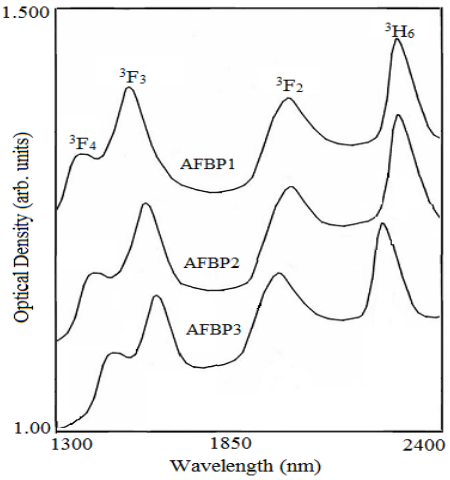

Fig. 4 Optical absorption spectra of Pr^{3+} doped alkali fluoroborophosphate glasses in near infrared region

Table 3 Judd-Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) and the spectroscopic Quality factor (Ω_4/Ω_6) of Pr^{3+} ions in alkali fluoroborophosphate glasses

Judd-Ofelt parameters (x10^{-22} cm²)	Glass		
	AFBP1	AFBP2	AFBP3
Ω_2	68.48	171.42	442.36
Ω_4	580.42	642.48	484.28
Ω_6	192.48	210.38	348.18
Spectroscopic Quality factor (Ω_4/Ω_6)	3.015	3.054	1.391

Therefore the variations of Ω_2 indicating that there is an increase in degree of disorder with replacement of alkali fluoride, and the lower values of Ω_2 suggests higher concentration of dangling bonds or lower degree of network connectivity. The higher Ω_2 parameter is observed in AFBP3 glass, is the indicator of the covalent character of the chemical bonds surrounded by the glass matrix and Pr^{3+} ions [24, 25].

3.5 Luminescence Studies

Figs. 5 and 6 shows the excitation and emission spectra of present glasses. From the recorded luminescence spectra, the emission levels $^3P_1 \rightarrow {}^3F_3, {}^3H_5, {}^3P_0 \rightarrow {}^3H_4$ and $^1D_2 \rightarrow {}^3H_4$ have been identified. In order to predict the performance of Pr^{3+} doped alkali fluoroborophosphate optical glasses, the radiative properties for $^1D_2 \rightarrow {}^3H_4$ emission state has been evaluated by the use of Judd-Oflet parameters obtained from the absorption measurements. The spontaneous emission probability value from the

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observed state to their next order lying state was estimated and the transition probability (A), total transition probability (A_T), and branching ratio (β_r) for the laser transition $^1D_2 \rightarrow {}^3H_4$ are also calculated from standard procedure and presented in Table 4. An examination of the data presented in Table 5 confirms that AFBP2 glass has got maximum β_r values compared to the other two glasses. It has already been established that an emission level with the β_r value near 0.5 becomes a laser emission transition.

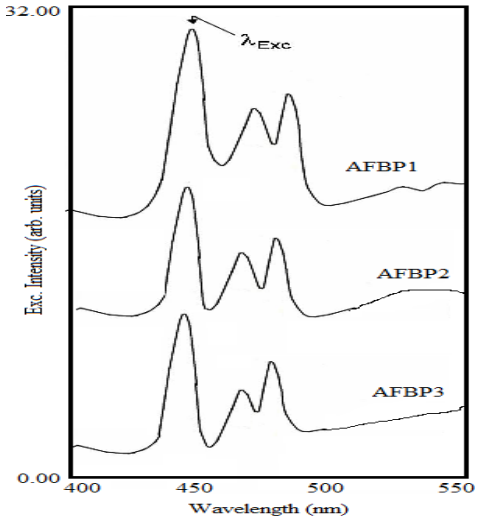

Fig. 5 Excitation spectra of Pr^{3+} doped alkali fluoroborophosphate glasses

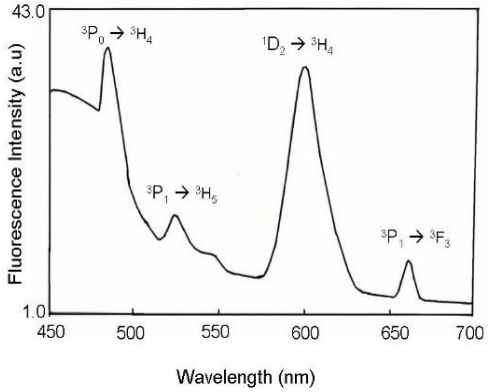

Fig. 6 Emission spectrum of Pr^{3+} doped alkali fluoroborophosphate glass (AFBP3)

Table 4 Radiative properties of Pr^{3+} doped alkali fluoroborophosphate glasses

Emission transition $^1D_2 \rightarrow$	Glass AFBP1		AFBP2		AFBP3	
	A (S^{-1})	βr (%)	A (S^{-1})	βr (%)	A (S^{-1})	βr (%)
$^1G_4$	114.84	7.16	132.82	7.37	320.48	11.77
$^3F_4$	220.24	13.74	412.26	22.86	958.12	35.19
$^3F_3$	56.48	3.52	64.46	3.58	103.18	3.79
$^3F_2$	384.42	23.98	324.28	17.99	412.48	15.15
$^3H_6$	364.82	22.76	312.18	17.31	298.49	10.96
$^3H_5$	19.19	1.20	14.86	0.824	19.48	0.715
$^3H_4$	442.58	27.61	542.18	31.10	610.84	22.43
$A_T = \Sigma A$	1603		1803		2723	

Table 5 Laser emission characteristics of Pr^{3+} doped alkali fluoroborophosphate glasses for $^1D_2 \rightarrow {}^3H_4$ transition

Property	Glass AFBP1	AFBP2	AFBP3
Radiative life time τ_R(μs)	623	555	367
Branching ratio βr (%)	27.61	31.10	22.43
Stimulated emission cross section σ_{Se} (10^{22} cm^2)	17.53	27.46	25.40

Because β_r value is better in AFBP2 for $^1D_2 \rightarrow {}^3H_4$ emission level, the system could be identified as a suitable one for laser action. Based on the magnitude of β_r values, the glasses are arranged as AFBP2 > AFBP1> AFBP3. From the luminescence spectral profiles, the stimulated emission cross-section σ_{se} for the transition $^1D_2 \rightarrow {}^3H_4$ is computed. The values of laser characteristics such as radiative lifetime, branching ratio and stimulated emission cross-section for $^1D_2 \rightarrow {}^3H_4$ transition for all the glasses are given in Table 5. The stimulated emission cross-section (σ_{se}) is found to be maximum for glass AFBP2, suggesting that glass AFBP2 is better compared to the other two glass systems.

4. Conclusion

To examine the effects of alkali fluorides three newly synthesized Pr^{3+} doped fluoroborophosphate glasses were prepared and characterized for their physical, absorption and luminescence properties at room temperature. From the absorption spectra, Judd-Ofelt parameters were evaluated and in turn were used to evaluate radiative lifetimes of lasing transition $^1D_2 \rightarrow {}^3H_4$. The Judd-Ofelt theory of electric dipole transition combined with the luminescence data has provided a convenient way to determine the laser properties of Pr^{3+} doped fluoroborophosphate glasses. The laser efficiency factors such as (β_r) and (σ_{se}) have confirmed that among the three glasses studied here, the AFBP2 glass with 20 mole% sodium could be identified as a suitable optical device for laser emission characteristics.

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