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Impact of Bi_2O_3 on structural properties and lasing effects in Nd^{3+} doped bismuth phosphate glasses at 1.053 μm emission

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ABSTRACT

Influence of addition of bismuth oxide (Bi_2O_3) on structural and optical properties of $0.5Nd^{3+}$ doped different phosphate glasses prepared by melt quenching technique were reported. The structural properties were analysed by FT-IR and ^{31}P MAS NMR techniques. ^{31}P NMR results showed that, with the variation of Bi_2O_3 concentration in the prepared phosphate glass matrices there was no significant change in the structure. The optical properties have been analysed using Judd–Ofelt (J-O) theory. From absorption spectra, three phenomenological J–O intensity parameters (Ω_2, Ω_4, Ω_6) have been calculated and these parameters were used to estimate the radiative properties. The J-O intensity parameters increased with increase in the concentration of Bi_2O_3, which confirmed the higher covalency, asymmetry and rigidity. The branching ratios (β) and emission cross-sections (σ) were calculated from the emission spectra of Nd^{3+} doped bismuth phosphate (BiP) glasses. Among different glass matrices 15 mol% of Bi_2O_3 glass matrix has higher β and σ values which are useful for the laser applications. The improved emission cross-section value with the addition of Bi_2O_3 content results low threshold and high gain applications. The decay curves of all these BiP glasses showed single exponential behaviour.

1. Introduction

Due to the importance of lasers in various fields, an extensive research work has been carried out on the development of rare earth (RE) ion doped laser glasses. The optical properties of RE ions in glasses strongly depend on the chemical composition of the glass matrix which determines the structure and nature of the glasses [1]. Solid state lasers operating in the near infrared (NIR) region have important applications in the fields such as optical communication, radar and medical instrumentation [2]. Among all RE ions, Neodymium (Nd^{3+}) is one of the utmost efficient lasing ion due to its multiple absorption levels spreading from Ultraviolet (UV) to NIR through visible spectral range for efficient pumping; high stimulated emission cross-section at ~1.06 μm and specific energy level structure which is ideal for low-threshold four-level lasers [3]. For example, in Nd: YAG single-crystal fiber achieved a continuous wave (CW) laser power of 10 W at 1064 nm for an incident pump power of 60 W at 808 nm and 360 kW peak power for 12 ns pulses at 1 kHz in the Q-switched regime [4] and in Nd: YAG ceramic rod, using a high-power virtual point source (VPS) laser diode (LD) pumping system, 31 W CW laser output at 1064 nm was obtained using 214.5 W/808 nm pump power [5].

Phosphate glasses are scientifically as well as technologically significant materials on account of their top-notch physical properties such as high thermal expansion coefficient, low melting and softening temperatures, UV transmission and good optical characteristics [6]. These properties make them useful for fast ion conducting material and other important applications, such as laser hosts, glass-to-metal seals and bio-compatible materials [7]. Phosphate glasses have unique properties that make them useful for a wide range of technical applications and these glasses have a relatively poor chemical durability [8], such as hygroscopicity and volatility which often limits their usefulness. The hygroscopicity and volatility arise mainly because of the presence of phosphorous structural units with non-bridging oxygen atoms, which can react with moisture, forming phosphoric acid. Phosphoric acid thus formed is detrimental to the glass and it volatilizes on heating [9]. However, by addition of heavy metal oxides like bismuth oxide (Bi_2O_3), lead oxide (PbO), aluminium oxide (Al_2O_3), tungsten oxide (WO_3), molybdenum oxide (MoO_3) etc. to the P_2O_5 network, increases cross-link density of the glass network which is responsible for improved chemical durability and physical properties [4]. Addition of heavy metal oxide modifiers in the host matrix increases the radiative parameters. In addition, heavy metal containing glasses reduce phonon energy and result into an increase in the quantum efficiency of luminescence from excited states of rare earth ions.

Bismuth oxide is a conditional glass former, but cannot form glass independently. Still with the addition of conventional glass formers such as phosphate, borate, silicate, tellurite etc., bismuth oxide forms the glass. Bismuth phosphate (BiP) glasses are of great interest because of their wide applications in optics and opto-electronic devices [4,10,11]

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due to wide glass formation range, high physical and chemical stability etc. In Bi_2O_3 based glasses, bismuth ions appear in [BiO_n] polyhedral such as BiO_3 pyramidal and BiO_6 octahedral units [12]. Due to its dual role, as modifier with [BiO_6] octahedral and glass former with [BiO_3] pyramidal units, Bismuth oxide occupies both network-forming and network-modifying positions [13]. Pal et al. investigated the effect of Bi_2O_3 in zinc bismuth borate glasses in which Bi_2O_3 acted as network modifier [14–16]. In the present work, Bi_2O_3 occupied network-forming positions.

In the present work, due to individual applications of phosphate, bismuth oxide and neodymium oxide, some bismuth phosphate (BiP) glasses doped with Nd^{3+} ions were prepared. The obtained samples were investigated by changing the composition of Bi_2O_3 (network modifier) using FT-IR, ^{31}P solid state NMR, absorption, photoluminescence (PL) and decay lifetime measurements. The aim of the present work is to study the structural and laser spectroscopic properties of Nd^{3+} doped different BiP glasses based on Judd-Ofelt (J-O) theory.

2. Experimental

2.1. Glass Preparation

The set of bismuth phosphate (BiP) glasses were prepared according to the molar composition $(79.5 - x)P_2O_5 + 10Li_2O + 10Na_2O + 0.5Nd_2O_3 + xBi_2O_3$ where: x = 0; 5; 10; and 15 mol%; were prepared by the conventional melt quenching technique using analar (AR) grade ammonium dihydrogen phosphate ($NH_4H_2PO_4$), bismuth oxide (Bi_2O_3), sodium carbonate (Na_2CO_3), lithium carbonate (Li_2CO_3) and neodymium oxide (Nd_2O_3) as starting materials. Reagents of 99.9% purity were used. About 10 g of batch composition was thoroughly ground in an agate mortar and this substance was taken into a porcelain crucible and heated in an electric furnace at 1150 °C for 1 h 30 min. The melt was quenched by pouring it onto a preheated brass mould and then allowed to cool to room temperature (RT) to obtain glass samples. Depending on different bismuth oxide compositions, the prepared glass samples are categorised in the following list:

1. Bi-0: $79.5P_2O_5 + 10Li_2O + 10Na_2O + 0.5Nd_2O_3 + 0Bi_2O_3$.
2. Bi-5: $74.5P_2O_5 + 10Li_2O + 10Na_2O + 0.5Nd_2O_3 + 5Bi_2O_3$.
3. Bi-10: $69.5P_2O_5 + 10Li_2O + 10Na_2O + 0.5Nd_2O_3 + 10Bi_2O_3$.
4. Bi-15: $64.5P_2O_5 + 10Li_2O + 10Na_2O + 0.5Nd_2O_3 + 15Bi_2O_3$.

2.2. Measurements

The density of fabricated glass samples was measured using Archimede's principle with water as immersion liquid. Refractive index (n) measurements were performed using an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromo naphthalene ($C_{10}H_7Br$) as contact liquid.

The Fourier transform infrared spectra were recorded at room temperature with 4 cm^{-1} spectral resolution between 400 and 4000 cm^{-1} on a BRUKER FTIR spectrometer. Solid state ^{31}P MAS NMR spectra were obtained at 400 MHz using a JOEL ECX400 DELTA2 NMR spectrometer with a 4 mm probe. The acquisition time was 18 ms and pulse width was 2.9 μs. The ^{31}P NMR spectra were collected in 128 scans, 5 s relaxation delay.

The optical absorption spectra were recorded using ELICO SL 218 double beam spectrophotometer. The fluorescence spectra in the range of 850–1400 nm were recorded with FL920, Edinburg using xenon lamp as excitation source.

3. Results and Discussion

3.1. Physical Properties

The density (D) and molar volume (V_m) of the 0.5 mol% Nd^{3+} doped different BiP glasses along with other physical parameters such as bismuth ion concentration (N), inter-nuclear separation (r_i), polaron radius (r_p) and field strength (F) were calculated by using standard relations [17] and they were listed in Table 1. The density of glass is used to explore the strength of the oxide material. This gives information about the structural compactness, interstitial spaces and coordination number [18]. The variation of measured densities and molar volumes with bismuth variation of the prepared glass samples is shown in Fig. 1. Both the density and molar volume of the glass samples increased with increasing bismuth content. The increase in density is due to the replacement of low density phosphorous element (1.823 $g \cdot cm^{-3}$) with high density bismuth element (9.781 $g \cdot cm^{-3}$). The increase in the molar volume is due to the larger values of the radii and bond length of Bi_2O_3 compared to those of P_2O_5, resulting in the formation of excess free volume, which increases the overall molar volume of the glasses [19]. It is observed from the Table 1 that, there is a considerable decrease in the inter-nuclear distance from 13.26 to 9.27 Å and polaron radius from 5.34 to 3.73 Å with the increase of Bi_2O_3 content from 5 to 15 mol% is ascribed to the congestion of Bi_2O_3 in the glass host [20]. The significant enhancement of field strength from 29.1×10^{15} cm^{-2} to 59.6×10^{15} cm^{-2} is observed and it is due to the occurrence of strong link between the bismuth and phosphate ions [20]. Hence from this it can be concluded that with increase of Bi_2O_3 concentration, inter-nuclear distance and polaron radius decreased thereby field strength increased.

3.2. Fourier Transform Infrared (FTIR) Spectra

In order to investigate the presence of structural units and functional groups in prepared glass samples, FTIR spectra of 0.5 Nd^{3+} doped BiP glasses were recorded and were shown in Fig. 2. The FTIR spectra of these glass matrices are analysed in the range 600–3900 cm^{-1}. Each infrared spectrum revealed several absorption bands localized at 725, 963, 1372, 1453–1464, 2815–2859, 2920 and 3744 cm^{-1}. The attributions of the absorption bands were done by the comparison of our results with data given in the literature and the following observations were identified:

(A) The band at 725 cm^{-1} was assigned to symmetric stretching vibration of P—O—P linkages.
(B) The band at 963 cm^{-1} was related to the asymmetric stretching vibrations of P—O—P linkages [21].
(C) The band at 1372 cm^{-1} was due to the asymmetric vibration of P—O bond in PO_4 groups.
(D) The band at 1737 cm^{-1} was related to H_2O bending vibrations [22].

Table 1
Density (D), molar volume (V_m), bismuth ion concentration (N), inter-nuclear separation (r_i), polaron radius (r_p) and field strengths (F) of 0.5 mol% Nd^{3+}-doped different bismuth phosphate (BiP) glasses.

Sample code	Mol% (x)	D ($g \cdot cm^3$)	V_m (cm^3/mol)	N (10^{20} ions/cm^3)	r_i (Å)	r_p (Å)	F × 10^{15} cm^{-2}
Bi-0	0	2.92	69.37	0	0	0	0
Bi-5	5	3.05	70.28	4.28	13.26	5.34	29.1
Bi-10	10	3.16	71.56	8.41	10.59	4.26	45.7
Bi-15	15	3.30	72.10	12.52	9.27	3.73	59.6