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Optical properties of Ho^{3+} ions in lead phosphate glasses

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ABSTRACT

Ho^{3+}-doped lead phosphate ($P_2O_5 + K_2O + Al_2O_3 + PbO + Na_2O + Ho_2O_3$) glasses have been prepared by conventional melt quenching technique. The optical properties have been characterized through absorption, emission and gain spectra and decay rate analysis. A strong dependence of the Ω_2 parameter on the hypersensitive transition has been noticed. Using the Judd-Ofelt intensity parameters, various radiative properties like transition probabilities, branching ratios and radiative lifetimes for various emission levels has been evaluated. The radiative lifetime for the ${}^5S_2({}^5F_4)$ fluorescent level and peak stimulated emission cross-section for the ${}^5S_2({}^5F_4) \rightarrow {}^5I_8$ transition are found to be 330 μs and 1.43×10^{-20} cm^2, respectively. Using the McCumber theory, absorption and emission cross-sections for the ${}^5I_7 \rightarrow {}^5I_8$ transition (~2.0 μm) of the Ho^{3+} ion have been obtained and gain spectra are also computed as a function of population inversion. The peak stimulated emission cross-section and gain coefficient for Ho^{3+}-doped lead phosphate glasses have been compared with other reported Ho^{3+}:systems. The analysis indicates that these Ho^{3+}:glasses exhibit relatively better properties for application in mid-infrared lasers at a wavelength of about 2.0 μm.

1. Introduction

Glasses and crystals activated with rare earth (RE) metal ions are still attractive as an active media for solid state lasers operating in the visible to infrared (IR) spectral ranges, fiber lasers, optical amplifiers due to their wide applications in laser remote sensing, telecommunications, atmosphere transmission, Raman laser amplifiers, optical parametric oscillators, eye-safe lidar and biomedical applications [1–6].

However, the advantage of glasses is, it is easy to produce large homogeneous pieces having low nonlinear refractive indices with large doping concentration. Typically, oxide glasses have more stable and harder [7]. Among the oxide glasses, phosphate glasses have several advantages over conventional silicate and borate glasses such as high transparency, low melting point, low refractive index and low dispersion and high ultraviolet transmission [8]. These properties make the phosphate glass as an attractive material for device fabrication. Addition of heavy metal oxide (PbO) is expected to make these glasses more moisture resistant, high thermal/chemical stability due to its dual role: one as a modifier and the other as a glass former. Presence of Al_2O_3 in oxides enhances the mechanical strength, gives greater chemical durability, lowers the coefficient of thermal expansion and increases freedom from devitrification. However, too much alumina increases the viscosity of glass, making it difficult to melt and work, whereas K_2O lowers the melting temperature to a manageable level and addition of Na_2O reduces the viscosity of the melt [9,10].

Among RE^{3+} ions, the Ho^{3+} is one of the interesting ions for spectroscopic studies. Because, it exhibits several electronic transitions in the visible and IR regions, which have relatively long-lived ${}^5I_7$ level and large peak stimulated emission cross-sections [11,12]. It has been demonstrated that infrared laser emission of the Ho^{3+} ion is in the range of 1.2–4.9 μm [13,14]. In addition to that, the Ho^{3+} ion provides eye-safe potential laser emission even at room temperature (RT) with a low threshold action that has attractive applications in atmospheric communication systems [15]. Moreover, the ${}^5S_2({}^5F_4) \rightarrow {}^5I_8$ transition of Ho^{3+} ion is a hypersensitive transition hence it is host dependent one. Therefore, it is expected that glasses doped with Ho^{3+} ions are the important candidates for both ~547 nm (${}^5S_2({}^5F_4) \rightarrow {}^5I_8$) and ~2 μm (${}^5I_7 \rightarrow {}^5I_8$) emissions which are useful for the development of visible and IR solid state lasers, respectively.

2. Experimental details

Ho^{3+}-doped lead phosphate glasses (PKAPbNHo) of molar composition:44 $P_2O_5 + 17$ $K_2O + 9$ $Al_2O_3 + (24-x)$ $PbO + 6$ $Na_2O + x$ Ho_2O_3, where $x = 0.1$, 0.5, 1.0 and 2.0 mol%, referred as PKAPbNHo01, PKAPbNHo05, PKAPbNHo10 and PKAPbNHo20, respectively, have been prepared by conventional melt quenching technique using the reagent grade $Al(PO_3)_3$, KPO_3, PbO, Na_2CO_3

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and Ho_2O_3 as starting materials. About 20 g of the batch composition was thoroughly crushed in an agate mortar and this homogeneous mixture was taken into a platinum crucible and melted in an electric furnace between 1100 °C and 1150 °C for 90 min. The melt was poured onto a preheated brass mould and annealed at 370 °C for 12 h to remove thermal strains and then cooled to RT. Afterwards, these glass samples were polished to attain good transparency and flat surfaces for optical measurements.

The density was measured by Archimedes' principle using water as an immersion liquid. Refractive index measurements were performed using an Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonapthalene ($C_{10}H_7Br$) as a contact liquid. The physical properties of PKAPbNHo10 glass are presented in Table 1. The absorption spectrum has been measured using Perkin Elmer Lambda-950 spectrophotometer in the range of 330–2400 nm. The 488 nm line of Ar^+ laser is used as an excitation source to record the photoluminescence spectra. The lifetime measurements are carried out using a mechanical chopper with a multi-channel scalar interfaced to a personal computer that recorded and averaged the signal.

3. Results and discussion

3.1. Absorption spectrum

The absorption spectrum of PKAPbNHo10 glass recorded in the wavelength range of 330–2400 nm at RT is shown in Fig. 1. The assignments of the absorption bands originating from the ground $^5I_8$ level to various excited levels within the 4*f* shell are also shown in Fig. 1. The observed absorption bands of Ho^{3+} ions are centered at 1945, 1154, 890, 641, 543, 538, 486, 473, 468, 454, 447, 418, 386, 382 and 361 nm and are attributed to the 4*f*–4*f* transitions of Ho^{3+} ions from the ground $^5I_8$ level to the different excited $^5I_7$, $^5I_6$, $^5I_5$, $^5F_5$, $^5S_2$, $^5F_4$, $^5F_3$, $^5F_2$, $^3K_8$, $^5G_6$, $^5F_1$, $^5G_5$, $^5G_4$, $^3K_7$ and $^3H_6$ levels, respectively. The location and assignments of the bands involved in $4f^{10}$–$4f^{10}$ transitions have been made and analysed by means of free-ion Hamiltonian (H_{FI}) model [16–20] from the absorption and emission spectra following similar studies reported in our earlier work for Ho^{3+} ions in glasses [21].

3.2. Oscillator strengths and Judd-Ofelt analysis

Intensities of the absorption bands are usually expressed in terms of oscillator strengths (*f*) which are statistically weighted to account the degeneracy of the initial level. The experimental oscillator strengths (f_{exp}) of absorption bands originating from the ground level of a RE^{3+} ion have been evaluated by measuring the integrated areas under the absorption bands from the absorption spectrum by the expression [22,23]:

$$f_{exp} = \frac{2.303mc^2}{\pi e^2 N}\int \alpha(\upsilon)\,d\upsilon = 4.318\times10^{-9}\int \alpha(\upsilon)\,d\upsilon \qquad (1)$$

where *m* and *e* are the rest mass and charge of an electron, respectively, *c* is the velocity of light, *N* is the number of RE^{3+} ions per unit volume and $\alpha(\upsilon)$ is the molar absorptivity of the corresponding band at an energy υ (in cm^{-1}).

Table 1
Physical properties of PKAPbNHo10 glass.

Properties	PKAPbNHo10
Optical path length, l (cm)	0.268
Density, d (g/cm^3)	3.680
Concentration, N ($\times10^{20}$ ions/cm^3)	2.970
Refractive index, n	1.570

The Judd-Ofelt (JO) theory [22,24,25] has been used to estimate the intensities of intraconfigurational *f*–*f* transitions of RE^{3+} ions. According to the JO theory, the transition intensities are characterized by three phenomenological parameters known as JO intensity parameters, Ω_λ (λ = 2, 4 and 6), which depend on the local environment. The relative magnitudes of Ω_λ are useful to explain the bonding, symmetry and stiffness of the host matrices [26]. The calculated (f_{cal}) and experimental (f_{exp}) oscillator strengths along with absorption band positions (λ) and corresponding energy level terms are given in Table 2.

Among various absorption transitions of the Ho^{3+} ion, the absorption bands assigned to the $^5I_8 \to {}^3H_6$ and $^5I_8 \to {}^5G_6$ transitions centered at around 361 and 454 nm, respectively, are referred as hypersensitive transitions [27]. These transitions obey the selection rules $|\Delta S| = 0$, $|\Delta L| \leqslant 2$ and $|\Delta J| \leqslant 2$ and they are very sensitive to the surrounding environment of the RE^{3+} ion. The Ω_λ parameters for Ho^{3+} ions in several environments [7,12,28–37] along with present work are collected in Table 3. The Ω_λ parameters for PKAPbNHo10 glass are found to be $\Omega_2 = 8.68$, $\Omega_4 = 3.04$ and $\Omega_6 = 2.37$ ($\times10^{-20}$ cm^2) that follow the trend as $\Omega_2 > \Omega_4 > \Omega_6$, which is similar to the trends observed in oxyfluoride (Si based) [12], phosphate [28], gallium lanthanum sulphide [29], oxyfluoride tellurite [30] and Ba–Al–Ge [31] glasses and Lu_2SiO_5 crystal [32], whereas the dissimilar trends have been noticed in other Ho^{3+}:systems such as tellurite [33], oxyfluoroborate [7], Ga_2S_3–GeS_2–La_2S_3 [34] and PbO–Al_2O_3–B_2O_3 [35] glasses and $SrLaGa_3O_7$ [36] and YAG [37] crystals. Among the three Ω_λ parameters, Ω_2 is more sensitive to the environment of the RE^{3+} ion and in turn strongly depends on hypersensitive transition i.e., the larger the hypersensitivity of the transition, the greater will be the value of Ω_2.

The Ω_2 parameter indicates the covalence of the metal–ligand bond, whereas Ω_4 and Ω_6 indicate the rigidity of the host matrix [38,39]. The higher value of Ω_2 in the present glass suggests that Ho^{3+} ion experiences relatively higher covalence of the bond between Ho^{3+} ions and the surrounding ligands as well as lower symmetry of the coordination structure compared to other reported Ho^{3+}:systems [7,12,28–37]. On the other hand, Ω_4 and Ω_6 values depend on bulk properties such as viscosity and dielectric of the media and are also affected by the vibronic transitions of the RE^{3+} ions bound to the ligand atoms [40].

3.3. Radiative properties and emission spectra

The radiative transition probability (A_R), radiative lifetime (τ_R) and branching ratio (β_R) which predict the fluorescence intensity of the lasing transition have been calculated using the Ω_λ parameters along with the refractive index (*n*) [41–43].

Fig. 2 shows the normalized emission spectra of Ho^{3+}-doped lead phosphate glasses recorded in the wavelength range of 500–800 nm. The emission bands centred at around 547, 661 and 756 nm are assigned to the transitions corresponding to the $^5S_2(^5F_4) \to {}^5I_8$, $^5F_5 \to {}^5I_8$ and $^5S_2(^5F_4) \to {}^5I_7$, respectively, of the Ho^{3+}:PKAPbNHo glass. Fig. 3 shows the partial energy level diagram of Ho^{3+} ion in the present glass along with excitation and emission channels.

The peak stimulated emission cross-section ($\sigma_e(\lambda_p)$) between ψJ and $\psi' J'$ levels is given as [43]:

$$\sigma_e(\lambda_p) = \left(\frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}}\right) A(\psi J, \psi' J') \qquad (2)$$

where λ_p and $\Delta\lambda_{eff}$ are the peak wavelength and effective bandwidth of the fluorescence line, respectively. The $\Delta\lambda_{eff}$ can be calculated by integrating the intensity of the fluorescence line shape and dividing by the intensity at the λ_p using the relation: