

Photoluminescence Studies of Pr³⁺ Doped Lead Germanate Glass

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Abstract The Pr³⁺doped PbO-GeO₂ glass samples have been synthesized by melting and quenching process. The nephelauxetic ratio, covalency and bonding parameter which provides the information about the type of bonding between the rare earth ion and neighbor oxygen atoms calculated. The optical parameters such as radiative transition probabilities, radiative lifetime, branching ratios etc. of Pr³⁺ ions have been determined by Judd-Ofelt analysis. An upconversion emission using the excitation at ~594 nm supported by energy transfer process due to dipole-dipole interaction in the ¹D₂ metastable state has been found.

Keywords Oscillator strength · Judd-ofelt formalism · Nephelauxetic ratio · Covalency · Bonding parameter · Upconversion · Energy transfer · Dipole-dipole interaction

Introduction

The study of triply ionised lanthanides doped glasses are of great importance due to wide application in many opto-electronic systems [1]. The electronic configuration of Pr³⁺ ion is [5s²5p⁶4f²]. The electric dipole interaction creates the LS terms viz. 3H, 3F, 1G, 1D, 1I, 3P and 1S etc. while the spin orbit interaction splits the LS terms into J levels and the ligand field splits the J levels. Due to the symmetry and strength of the ligand field, Pr³⁺ ion generates several metastable states. The presence of long lived energy levels of Pr³⁺ ions doped in different hosts

provide the information of radiative emissions in some visible and infrared regions [2].

Every host doped with Pr³⁺ ions presents particular aspects and complexities. Trivalent praseodymium ion doped glass and crystal hosts are really a special entity which can be applied as a theoretical tool for explaining the observed data and pointing the satisfactory picture in right direction. The optical properties of lanthanide ions doped in different glasses have been examined and their spectroscopic properties such as absorbance, fluorescence, upconversion etc. have been reported by several workers [3–14]. Heavy metal oxide glasses doped with rare earth ions are mostly suitable candidates for the better performance of the optical properties [7–13]. Among these, the lead germanate glasses are very suitable due to some important characteristics namely, lower cutoff phonon frequency (~700 cm⁻¹), high refractive index (~1.9), large transmission range (400–4500 nm), non-hygroscopy in nature etc. [7, 8, 11]. Luminescence in lead germanate glasses with doping concentrations of 0.05 and 0.5 mol% of Pr³⁺ compounds have been shown in visible regions [7, 8]. Heavy metal oxide glassy materials codoped with Pr₆O₁₁ and silver nanoparticles have been examined on the basis of optical absorbance and luminescence spectra due to the surface plasmons interaction [9, 10]. Upconversion emissions in Pr³⁺ ion doped in TeO₂-PbO-GeO₂ glasses using a 520 nm laser excitation have been reported [11]. Frequency upconversion in Pr³⁺ doped tellurite glasses under the excitation with a near infra red (NIR) laser due to excited state absorption (ESA) have been observed throughout the visible region [12]. The stokes luminescence and frequency upconversion emissions in Pr³⁺ doped TeO₂-PbO glass samples upon pulsed dye laser excitation have been reported and described in detail by Rai et al. [13].

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In this paper, we report the spectroscopic studies of triply ionised praseodymium incorporated in lead germanate glass samples using Judd-Ofelt (J-O) analysis. The mechanism responsible for the frequency upconversion emission has been explained and the various parameters viz. nephelauxetic ratio, covalency, bonding parameters etc. have been determined.

Experimental

The Pr^{3+} incorporated lead germanate glass samples with compositions of $51\text{PbO}-49\text{GeO}_2$ (in mol%) were fabricated by fusing and quenching method. The doping amount of Pr_2O_3 were 0.2, 0.4, 0.6, 0.8, 1.0 mol%. The reagents in powder form were crushed and mixed in an agate mortar to get homogeneous mixture and melted in an alumina crucible at $800\text{ }^\circ\text{C}$ for 1 h, quenched inside a brass mold, annealed at $380\text{ }^\circ\text{C}$ for 30 min. and then cooled to room temperature ($28\text{ }^\circ\text{C}$). The samples of good optically transparent quality were taken for the optical experiment after cleaning and polishing. The refractive index of samples were determined (~ 1.9) with the help of Brewster angle polarisation method. A 2 mW He-Ne polarized laser was used for this purpose. The optical absorption spectra of 1.0 mol% of Pr^{3+} doped lead germanate glass sample was recorded using a Lambda-19-VIS-NIR double beam spectrometer. For the photoluminescence spectrum, we have used an excitation line of 594 nm from a dye laser pumped by the second harmonic of Nd: YAG laser (8 ns pulse, repetition rate ~ 5 Hz). The excitation beam was focussed vertically on the glass sample with the help of a lens of focal length 10.0 cm and the photoluminescence was collected in the direction perpendicular to the direction of incident beam. The signal was analysed by a spectrometer (~ 5 nm resolution) attached to a photomultiplier tube. All the optical experiments were performed at room temperature. Similar experiments were done for other samples one by one and found that sample with dopant amount 1.0 mol% shows almost good results in all optical experiments.

Results and Discussion

Judd-Ofelt Calculation

Judd-Ofelt theory [14, 15] has drawn an attention for calculations of radiation as well as absorption parameters in many rare earth doped systems. Present study of this theory signifies oscillator strengths, radiative transition probabilities, which suggests the possibilities of emissions from a certain excited state of rare earth ion. Figure 1a and b shows the absorption spectra of 1.0 mol% Pr^{3+} doped in

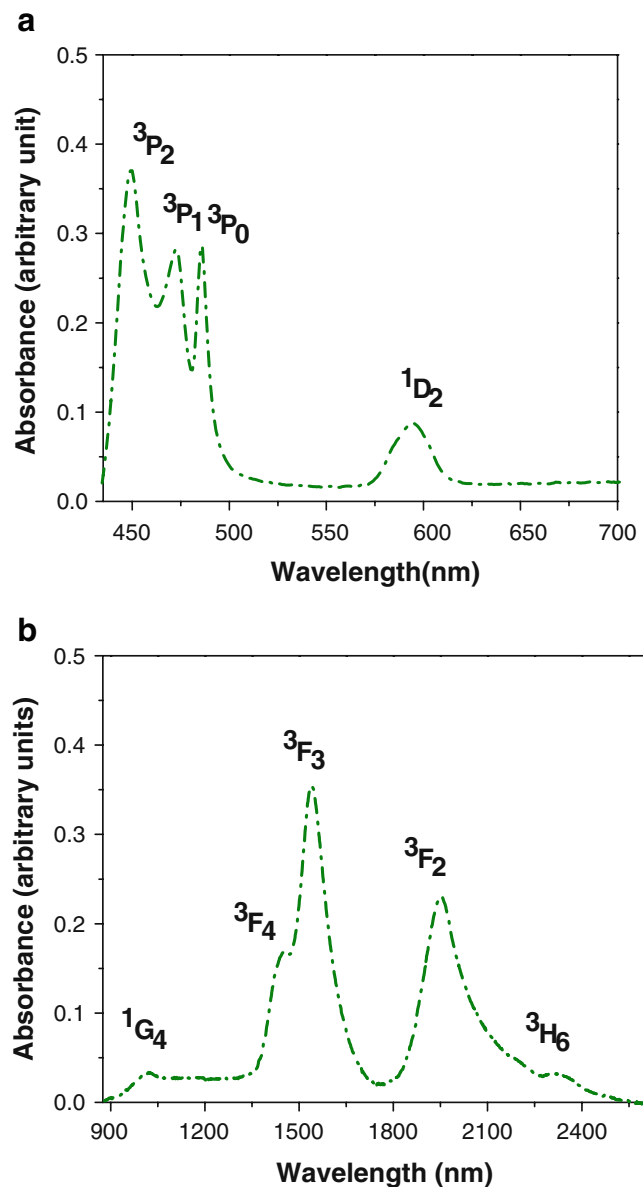


Fig. 1 **a** Absorption spectra of 1.0% mol Pr^{3+} doped in lead germanate glass in 400–700 nm. **b** Absorption spectra of 1.0% mol Pr^{3+} doped in lead germanate glass in 800–2700 nm

lead germanate glass sample in the region 400–2600 nm. The absorption bands are inhomogeneously broadened due to site to site variations in the crystal field strength. Similar spectra were obtained for all the doped samples with their relative intensities. The intensities of the absorption bands were found to exhibit the linear variation with the concentration of ions. The absorption spectra contains nine bands corresponding to the ground state to the different $^3P_{2,1,0}$; 1D_2 ; 1G_4 ; $^3F_{4,3,2}$; 3H_6 excited states centered at 22222.2, 21141.6, 20576.1, 16835.0, 9803.9, 6501.9, 5130.8, 4290.0 cm^{-1} respectively. The characteristic bands ($^3P_{2,1,0} \leftarrow ^3H_4$) in the blue regions have been observed with appreciable intensities. Similarly a broadband has been

observed in orange-red region. The experimental and calculated oscillator strengths for different absorption bands have been determined by using the following expressions.

$$F_{exp.} = \frac{mc^2 n^2}{\pi e^2 N \chi} \int K(\nu) d\nu \tag{1}$$

where $\int K(\nu) d\nu$ denotes area covered by corresponding absorption peaks.

$$F_{cal.} = \frac{8\pi^2 m \nu c}{3h(2J + 1)} \left[\frac{(n^2 + 2)^2}{9n} \right] S_{ed} \tag{2}$$

where J is the corresponding total angular momentum value of ground state of Pr³⁺ ion,

Electric dipole line strength

$$\begin{aligned} &= S_{ed}[(S, L, J); (S', L', J')] \\ &= \sum_{\lambda=2,4,6} \Omega_{\lambda} | \langle (S, L, J) || U^{\lambda} || (S', L', J') \rangle |^2 \end{aligned} \tag{3}$$

where ‘U^λ’ is the reduced matrix elements of Pr³⁺ free ion [16].

Comparing Eqs. (1) and (2), We have calculated Judd-Ofelt intensity parameters Ω₂, Ω₄ & Ω₆ and values of those trends as Ω₂<Ω₄>Ω₆. A resonable agreement between the oscillator strength values calculated experimentally and theoretically have been observed. Judd-Ofelt intensity parameters do not change with the concentration. The absorption spectra of rare earth ions doped hosts are main source to calculate the radiative parameters viz. spontaneous emission transition probabilities, total radiative transition probabilities, branching ratios and radiative lifetimes etc. The formulaes for above quantites are expressed as follows.

Radiative transition probability of a transition can be represented as,

$$A(\psi_J \rightarrow \psi_{J'}) = \frac{64\pi^4 \nu^3 n(n^2 + 2)^2 e^2}{3h(2J + 1)9} \cdot S_{ed} \tag{4}$$

where J and J’ are the corresponding values of initial higher and final lower states, ν is the difference in their energies.

Total transition probability of the excited state may be expressed as,

$$A_T(\psi_J) = \sum A(\psi_J \rightarrow \psi_{j'}) \tag{5}$$

Radiative lifetime (τ) of fluorescent level can be defined as,

$$\tau = \frac{1}{A_T(\psi_J)} \tag{6}$$

Branching ratio of each radiative transition can be calculated as,

$$\beta_r(\psi_J \rightarrow \psi_{j'}) = A(\psi_J \rightarrow \psi_{j'}) / A_T(\psi_J) \tag{7}$$

The above assignments of some transition are placed in (Table 1). The transition probabilities and branching ratios from ³P₁, ³P₀ and ¹D₂ excited states to ³H_{4,5} states are comparatively larger than other transitions. The largest value is corresponding to the ³P₀→³H₄ transition. The possibilities of above transitions may theoretically support the photoluminescence emissions in the visible region. The calculated radiative lifetimes of ³P₀ and ¹D₂ states are ~54.33 μs and 0.75 ms respectively.

Table 1 Radiative transition probabilities, total radiative transition probabilities, branching ratios and radiative lifetimes of ³P₂, ³P₁, ³P₀ and ¹D₂

SLJ S'L'J'	A(s ⁻¹)	β
³ P ₁ → ³ P ₀	0.04	0.00
¹ D ₂	16.26	0.00
¹ G ₄	296.68	0.04
³ F ₄	590.81	0.09
³ F ₃	638.74	0.10
³ F ₂	835.54	0.12
³ H ₆	974.20	0.15
³ H ₅	1423.00	0.21
³ H ₄	1923.70	0.29
A _T =ΣA=6698.97 s ⁻¹ , τ=149.28 μs		
³ P ₀ → ¹ D ₂	32.38	0.00
¹ G ₄	772.99	0.04
³ F ₄	1589.60	0.09
³ F ₃	1724.00	0.09
³ F ₂	2278.50	0.12
³ H ₆	2671.20	0.15
³ H ₅	3950.40	0.22
³ H ₄	5387.00	0.29
A _T =ΣA=18406.07 s ⁻¹ τ=54.33 μs		
¹ D ₂ → ¹ G ₄	32.97	0.03
³ F ₄	93.64	0.07
³ F ₃	104.63	0.08
³ F ₂	152.06	0.11
³ H ₆	187.25	0.14
³ H ₅	308.32	0.23
³ H ₄	452.52	0.34
A _T =ΣA=1331.39 s ⁻¹ τ=0.75 ms		

The Bonding between Pr^{3+} Ion and Oxygen Atom

The type of bonding between rare earth ion and oxygen atom can be determined by nephelauxetic ratio, bonding parameter and covalency. The nephelauxetic ratio (β^-) is regarded as measure of covalency and expressed mathematically as $\beta^- = \frac{1}{n} \sum \frac{\nu_{\text{complex}}}{\nu_{\text{freeion}}}$, where ‘ ν ’ and ‘ n ’ are wave number of an absorption transition of a rare earth ions (Pr^{3+}) and number of observed absorption transitions respectively [17–19]. The energy level positions of free rare earth ion have been taken from [16]. The covalency (δ) and bonding parameters ($b^{1/2}$) can be calculated by using the standard relations [20–22] as, $\delta = \frac{(1-\beta^-)}{\beta^-}$ and $b^{1/2} = \left[\frac{(1-\beta^-)}{2} \right]^{1/2}$, where the terms have their usual meanings. The respective values of β^- , δ and $b^{1/2}$ in present host matrix are observed to be 0.985, 0.015 and 0.087 (Table 2). The positive values of nephelauxetic ratio (<1), covalency and bonding parameters satisfy more the possibility of covalent bonding between the triply ionized rare earth ion and oxygen atom [23–25].

Upconversion Emissions

Figure 2 shows the photoluminescence spectra of Pr^{3+} doped in lead germanate glass sample (dopant conc. 1.0 mol%) in between 400–800 nm using the direct excitation into the $^1\text{D}_2$ state (594 nm). Two emission peaks, one at ~ 486 nm (Fig. 2a) and another at ~ 675 nm (Fig. 2b) have been observed. The emission centered at ~ 486 nm corresponds to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition and shows frequency upconversion in the blue region, while the emission at ~ 675 nm corresponding to the $^1\text{D}_2 \rightarrow ^3\text{H}_5$ transition exhibits downconversion (Stokes fluorescence) in the red region. Similar features with their relative intensity behaviour have been observed for the different Pr^{3+} doped lead germanate glass samples.

In order to enquire the required number of laser photons populating the emitting level, upconversion intensity as a function of laser intensity was measured. The upconversion

Table 2 The observed values for nephelauxetic effect (β^-), covalency (δ) and bonding parameters ($b^{1/2}$) for complexes of Pr^{3+}

S. No.	β^-	δ	$b^{1/2}$	Composition	Reference
1.	0.949	0.053	0.159	APAAA	[20]
2.	0.990	0.010	0.071	EDTA	[24]
3.	0.962	0.039	0.138	NTA	[20]
4.	0.964	0.038	0.135	TNO	[25]
5.	0.985	0.020	0.125	PGO	[Present work]

APAAA amino polycarboxylic acid acetyl acetone, EDTA Ethylene diamine tetra acetic acid, NTA nitrilo triacetic acid, TNO Tellurite sodium oxide

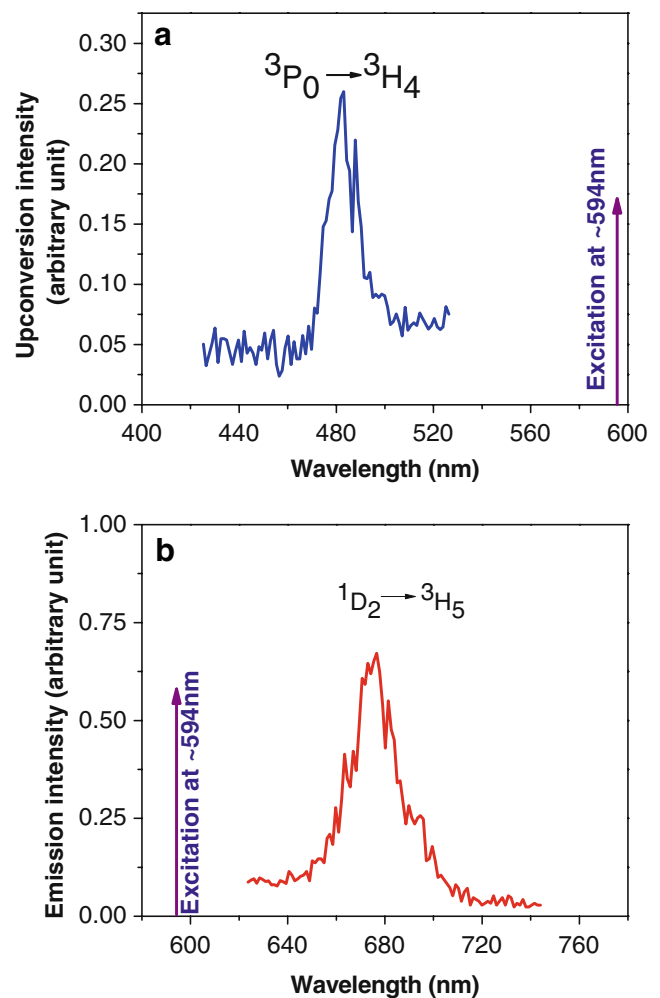


Fig. 2 a Upconversion spectra b Emission spectra of the sample with doping amount 1.0 mol% with an excitation of 594 nm

intensity is generally expressed as $(I_L)^n$, I_L being laser intensity and ‘ n ’ the number of laser photons required to populate the emitting level. A log-log plot variation of I_U with respect to I_L is shown in Fig. 3. The slope of the plot gives the value of n . In present case n is found to be 1.9, indicating that two photon process is involved in this upconversion emission. Similarly, for the fluorescence emission peaking at ~ 675 nm, a linear behaviour between the fluorescence intensity versus concentration of ions as well as laser intensity has been observed. As mentioned, we have prepared a number of doped lead germanate glass samples with different concentrations of dopant Pr^{3+} ions. It is observed that the upconversion intensity of emission band corresponding to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition increases with growing concentrations of dopants in lead germanate glass samples. The log-log plot between upconversion intensity and Pr^{3+} ion concentrations is found to be quadratic in behaviour and hence represents the two number of rare earth ions are participated in the frequency

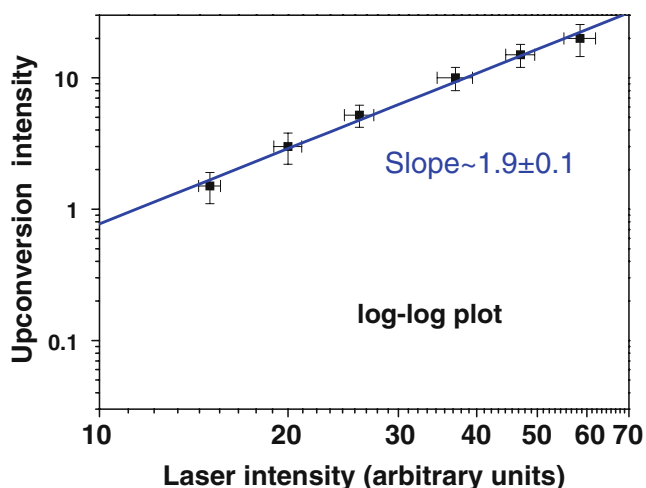


Fig. 3 Variation of upconversion intensity with Laser intensity for 1.0 mol%

upconversion process, whereas for the emission at ~675 nm, a linear variation between the emission intensity versus concentration of ions has been observed.

To clarify the knowledge of upconversion as well as fluorescence, it is very interesting to observe the schematic energy level diagram of Pr³⁺ ion (Fig. 4). The Pr³⁺ ions in the ground state absorb the photons of wavelength ~594 nm and get raised to the ¹D₂ excited state. Since the radiative lifetime of the ¹D₂ state is 0.75 ms, the large number of rare earth ions may be present in this state. Due to the interaction among the excited Pr³⁺ ions in the ¹D₂ state, energy exchange takes place. The donor ion in the ¹D₂ level de-excites to the lower levels via ¹G₄ level through the nonradiative transitions and finally decays to the ground state. The other ion, which gains energy jumps to the upper excited state. Fortunately, the ³P_J level allows this excited transition because of the matching of energy gap between the ¹D₂ and ³P_J levels. The highly excited rare earth ions

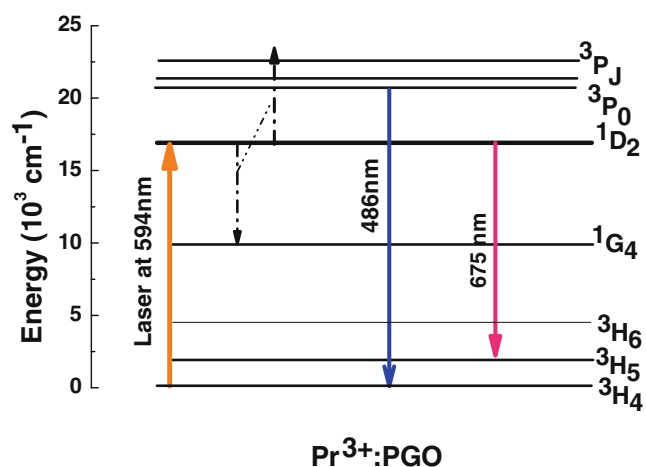


Fig. 4 Schematic energy level diagram of Pr³⁺ doped in lead germanate glasses for 1.0 mol%

come to the lowest state of ³P_J level (i.e. ³P₀) through the nonradiative relaxation. Since ³P₂, ³P₁, ³P₀ energy levels are lying at ~22222.2, ~21141.6 and ~20576.1 cm⁻¹ respectively and the present host material possesses the phonon energy of ~700 cm⁻¹, the decay of the ³P₂ level to ³P₀ level requires two phonons involved. Then it performs a radiative emission of ~486 nm corresponding to the ³P₀→³H₄ transition. This leads to orange to blue frequency upconversion of Pr³⁺ ion in the present host. This upconversion emission process must be energy transfer between two rare earth ions into the ¹D₂ state. This frequency upconversion path way was previously observed for the TPO glass [12]. As number of rare earth ions are pumped into the ¹D₂ state during the excitation corresponding to the ³H₄→¹D₂ transition and a pair of excited ions are participating in the upconversion and the ions, which are not responsible for the upconversion, may go to the ³H₅ state through a radiative transition showing a stokes luminescence at ~675 nm due to the ¹D₂→³H₅ transition. A linear behaviour for the intensity of stokes luminescence versus laser intensity as well as concentration of Pr³⁺ ions has been observed (Fig. 5).

To get the detail information about the type of interaction involved in the energy transfer process, the decay curve of the stokes luminescence at ~675 nm has been monitored and described by $I(t) = I_0 \exp[-t/\tau_0 - P(t)]$, where τ_0 is the lifetime of the ¹D₂ level in absence of energy transfer (~750 μs). P(t) is the function of time which involves different forms at different concentrations and mechanisms of interaction between ions. At long times when the acceptors at large distances are considered, the P(t) assumes the form $P(t) = \gamma t^{3/S}$ where S=6, 8, 10 for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. In the present case 3/S=ρ was found to be

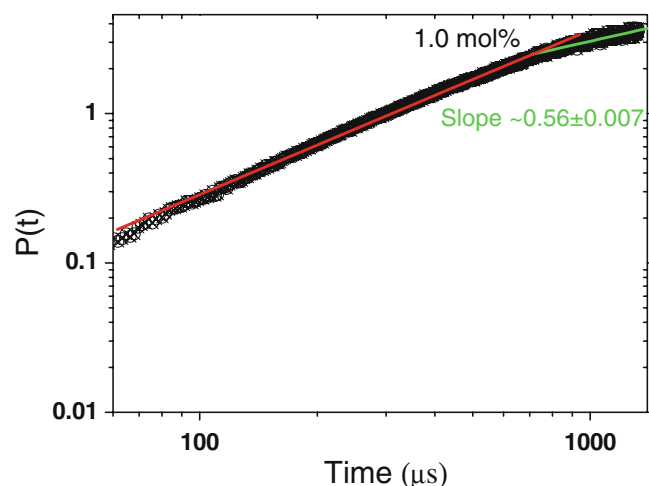


Fig. 5 log-log plot for P(t) versus t of 1.0 mol% of Pr³⁺ doped lead germanate glass

$0.45 < \rho \leq 0.56$. This signifies the interaction to be of dipole-dipole type.

Conclusion

The absorption and photoluminescence spectra of Pr^{3+} doped lead germanate glasses have been studied and its optical parameters like oscillator strength, transition probability, total transition probability, branching ratio etc. have been calculated. The positive values of nephelauxetic ratio, covalency and bonding parameter informs the possible existence of covalent bonding between the rare earth ion and surrounding oxygen atom. The upconversion emission observed in blue region has been confirmed due to the energy transfer among two excited ions in the $^1\text{D}_2$ state. The lead germanate glass due to its wide transmission range, high refractive index, long time durability, high mechanical strength etc. may be suitable for making the upconvertors.

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