



OPEN Near-infrared quantum cutting luminescence in $\text{Pr}^{3+}/\text{Yb}^{3+}$ doped lead bismuth borate glass

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In this paper, thermally stable lead-bismuth-borate glasses were doped with 0.5 mol% of Pr^{3+} ions at several concentration levels of Yb^{3+} ions. Structural characterizations were performed via Raman, differential scanning calorimetry, optical absorption and fluorescence spectra. The Judd–Ofelt intensity parameter, Ω_2 , of Pr^{3+} doped glass was comparatively higher than those from reported ones, which reflects the increase of co-valency and asymmetry of chemical bonds in the local environment of Pr^{3+} . Near-infrared emission in 900–2200 nm wavelength range was recorded through 443 nm blue laser pumping. Visible to near-IR quantum cutting and concentration quenching mechanisms were discussed to understand the luminescent behaviour. Intense IR emission ($\sim 1.0 \mu\text{m}$) features generated by absorbing one visible photon leads to quantum efficiencies close to 128% in $\text{Pr}^{3+}/\text{Yb}^{3+}$ co-doped samples which may improve the solar spectrum absorption and accordingly, increase the efficiency of c-Si solar cells. Emission cross-section, lifetime, figure of merit and gain bandwidth corresponding to $\text{Pr}^{3+}: {}^3\text{F}_2 \rightarrow {}^3\text{H}_4$ ($\sim 2.0 \mu\text{m}$) were comparatively reported suggesting that the glass with molar composition $0.5\text{Pr}^{3+}/0.1\text{Yb}^{3+}$ might be a potential candidate for $\sim 2.0 \mu\text{m}$ laser operation with low pump threshold.

Quantum cutting (QC) luminescence in materials doped with rare earth (RE) ions is an interesting subject towards the development of fluorescent tubes, plasma display panels and solar cells. In the quantum-cut optical phenomenon, two lower-energy photons are obtained by the energy partition of a high-energy photon. As a consequence, this process opens the possibility of its application in solar cells technology in order to enhance the efficiency of the latter via thermal loss prevention without structural change. Generally, spectra mismatch between solar spectrum and silicon band gap energy are the major gain limiter in c-Si solar cells. The low energy photons can not be absorbed effectively while high-energy photons were not used efficiently. The energy excess is lost in the form of heat during the thermalization of hot carriers¹. Therefore, the maximum efficiency of a c-Si solar cell is 33% obtained for a band gap of approximately 1.12 eV (1100 nm)^{1,2}. Solar efficiencies higher than 33% are also reported for multi-junction solar cells but are limited due to high cost and the requirement of high-quality contacts between the absorber materials while with physical and chemical matching properties³.

An alternative approach to enhance the solar cell efficiency is the rare earth (RE) co-doping with luminescent materials known to be efficient QC down-converters. These materials can absorb one UV-visible photon ($< 500 \text{ nm}$) and generate two IR photons that can be efficiently absorbed by the c-Si solar cells. The most common type of rare earth co-doped systems are $\text{Tm}^{3+}-\text{Yb}^{3+}$ ⁴, $\text{Er}^{3+}-\text{Yb}^{3+}$ ⁵, $\text{Tb}^{3+}-\text{Yb}^{3+}$ ⁶ and $\text{Pr}^{3+}-\text{Yb}^{3+}$ ⁷ where Tm^{3+} , Er^{3+} , Tb^{3+} and Pr^{3+} act as absorbing centers. The Yb^{3+} ions act as acceptors and their emitting light energy around 1000 nm is just above the band gap of c-Si solar cell⁴. Usually, in RE co-doped systems, the near-infrared (NIR) quantum cutting process involves the contribution of second-order cooperative energy transfer (CET) and first-order resonant energy transfer (ET) mechanisms. The latter one is more efficient than CET process but there is a possibility of high CET at higher Yb^{3+} ion concentrations^{4,7}. Recently, first-order, multiphoton, NIR quantum cutting in Er^{3+} , Tm^{3+} ions and $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped materials have been studied and proved to develop first-order, multi-photon QC germanium (Ge) and Silicon–Germanium (Si–Ge) solar cells (sensitive to 280–1850 nm) with efficiencies exceeding 38%⁸. $\text{Pr}^{3+}-\text{Yb}^{3+}$ co-doped systems have been also studied⁹ due to their efficient optical response in terms of QC phenomenon which can be explained from the emission of Yb^{3+} after resonant

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excitation of the Pr^{3+} : 3P_J levels. Van Wijngaarden et al.¹⁰ theoretically showed first-order resonant mechanism: $^3P_0 \rightarrow ^1G_4(\text{Pr}^{3+})$ to $^2F_{5/2} \rightarrow ^2F_{7/2}(\text{Yb}^{3+})$ or $^1G_4 \rightarrow ^3H_4(\text{Pr}^{3+})$ to $^2F_{5/2} \rightarrow ^2F_{7/2}(\text{Yb}^{3+})$ in LiYF_4 : $\text{Pr}^{3+}/\text{Yb}^{3+}$ crystals. Tanabe et al.¹¹ showed also a first order resonance energy transfer mechanism in $\text{Pr}^{3+}/\text{Yb}^{3+}$ co-doped oxyfluoride glass-ceramics. Moreover, Pr^{3+} with its rich spectrum of electronic levels involves a large number of optical transitions in the near- and mid-infrared wavelength range, which have potential uses in amplifiers, remote sensing, tissue welding, micro-surgery, environmental trace gas detection and spectroscopic applications.

In order to achieve efficient near- and mid-infrared emissions, low phonon energy of the host material is required to reduce probabilities of multiphonon relaxations between the electronic levels of RE^{3+} ions. Tellurite¹², germanate¹³, fluoride¹⁴ and chalcogenide¹⁵ glasses doped with RE ions are all promising systems for near- and mid-infrared lasers as they possess low phonon energy. Bi_2O_3 and PbO based heavy metal oxide (HMO) glasses also possess excellent IR transmission, low phonon energy, high refractive index and good corrosion resistance compared to other conventional oxide glasses. Generally, the B_2O_3 network former allows wider range of glass forming with heavy metal oxides (PbO , Bi_2O_3 and WO_3) than silicates, phosphates and tellurites. In this way, we have chosen lead-bismuth-borate glass composition, as host matrix, as they may exhibit excellent properties: high density, high refractive index, nonlinear refractive index, broad transmission window and low phonon energy^{16–19}. They are also stable, moisture resistant, have relatively low melting temperature and high polarizability (small field strength) of Bi^{3+} and Pb^{2+} cations. Such unique characteristics evince their potential applications in photonics, mechanical sensors, and reflecting windows^{20–22}.

In this work, lead-bismuth-borate host matrix were doped with Pr^{3+} and Yb^{3+} ions. While doped lead-borate, bismuth-borate and lead-bismuth-borate glasses have been extensively investigated for nonlinear and magneto-optic applications^{23–25}, fewer literature was reported concerning the topics of optical spectroscopy and laser applications. This paper investigates the influence of Yb^{3+} ions on near infrared quantum cutting luminescence (~ 1.0 & $2.0 \mu\text{m}$) in $\text{Pr}^{3+}/\text{Yb}^{3+}$ codoped glasses through 443 nm excitation. Moreover, it conducts investigations about radiative excited states lifetimes and about energy transfer mechanisms between Pr and Yb ions.

Results and discussion

Raman spectra of $\text{Pr}^{3+}/\text{Yb}^{3+}$ doped glasses excited by 633 nm laser and Gaussian fittings of the spectrum, are shown in Fig. 1a. There are ten fitted peaks located at $\nu \sim 121, 145, 184, 250, 392, 955, 1112, 1631, 1744$ and 1847 cm^{-1} , respectively. The most intense band at frequency $\sim 200 \text{ cm}^{-1}$ is associated to the vibration of heavy metal ions i.e., vibration involving motion of Bi^{3+} cations that are incorporated in the glass network as $[\text{BiO}_3]$ pyramidal and $[\text{BiO}_6]$ octahedral units^{26,27}. The 250 cm^{-1} can be attributed to the vibrations of Bi–O bonds²⁷. The broadband maxima at 392 cm^{-1} is due to Bi–O and Bi–O–Bi vibrations in distorted $[\text{BiO}_6]$ polyhedra²⁷. The bands around 955 and 1112 cm^{-1} arise by the symmetric stretching vibration of B–O bonds in $[\text{BO}_4]$ tri-, tetra- and penta-borate units²⁸. Their intensities constitute an overlap of B–O bonds with non-bridging oxygens (NBOs) in BO_4 units. The high frequency bands, $1631, 1744$ and 1847 cm^{-1} are associated to the stretching vibrations of the terminal B–O bonds of the pyro-borate units²⁸. It is worth to note that the observed decrease of the intense band maxima at low ($\sim 145 \text{ cm}^{-1}$) and high ($\sim 1744 \text{ cm}^{-1}$) frequencies with the increase of Yb^{3+} content, indicate decrease of Bi^{3+} cations in $[\text{BiO}_3]$ and $[\text{BiO}_6]$ units, and a decrease number of B–O bonds by the formation of B–O–B linkages in pyro-borate structural units.

Thermal property of the prepared glasses with addition of Yb^{3+} ions are analysed by DSC measurements and are shown in Fig. 1b along with glass transition temperature values. T_g is an important parameter to testify the glass thermal stability to resist thermal damage at high pump-power laser intensities for a laser glass. It can be seen that the increase of T_g with increase of Yb^{3+} ions from 451 to 487°C , indicates the enhancement of rigidity of the glass. This property could be beneficial for stabilization of the glass structure. Density is also a property that reveals the underlying structure of the glass. The density (d) increase of the glasses (see inset data in Fig. 1b) is interrelated with the increase in the packing degree of the glass structure with the increase of Yb^{3+} concentration.

Figure 2a displays the spectra of absorption of Pr^{3+} doped and $\text{Pr}^{3+}/\text{Yb}^{3+}$ co-doped glasses. The absorption bands of Pr^{3+} which correspond to transitions from the ground state 3H_4 to the excited levels are labeled

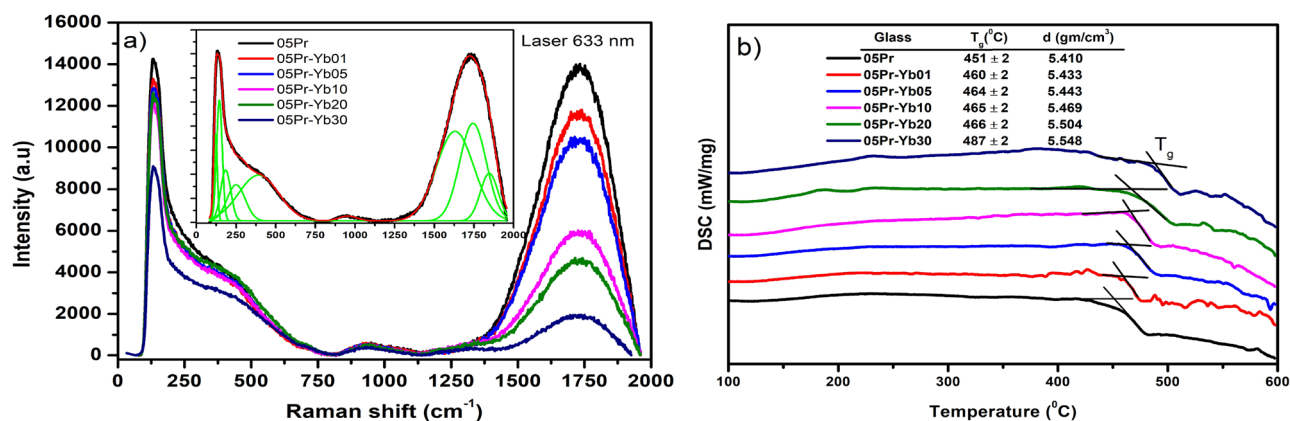


Figure 1. (a) Raman and (b) DSC spectra of glasses. Inset of (a) shows Gaussian fit.

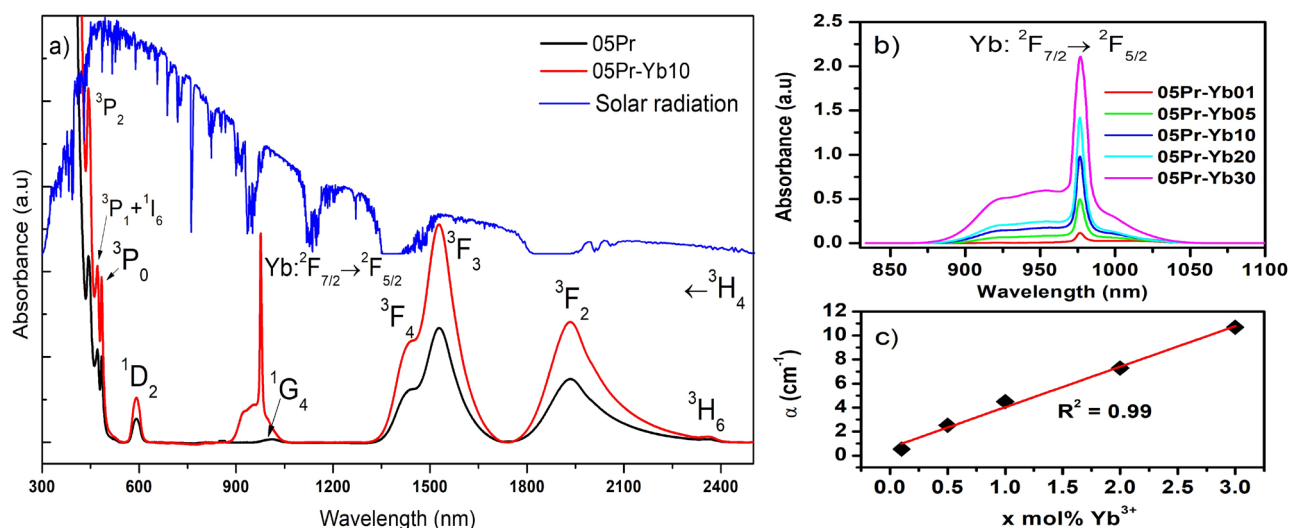


Figure 2. (a) Optical absorption spectra of Pr³⁺ singly doped and Pr³⁺/Yb³⁺ co-doped glasses, and sun radiation AM1.5 spectrum; (b) absorption intensity of Yb³⁺: $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition, and (c) integrated intensity of $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition as a function of Yb³⁺ ions.

in Fig. 2a. The absorption band around 1011 nm of Pr³⁺ is weak. Adding Yb³⁺ as co-dopant to Pr³⁺ leads to enhancement of the absorption around the range, 875–1065 nm, as well as, the presence of the strong Ytterbium absorption cross-section at 980 nm related to $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition, as labeled in Fig. 2a. This band intensity increases with Yb³⁺ content as shown in Fig. 2b and a linear variation of the absorption coefficient is verified in Fig. 2c, which is an indicative of Yb³⁺ ions solubility in the glass network, revealed by the linear fit ($R^2 = 0.99$). On the other hand, the absorption of Pr³⁺ in the blue-violet wavelength region is effective to absorb photons, which are not efficiently absorbed by the solar cells. Therefore, co-doping of Pr³⁺ and Yb³⁺ ions are not only applicable to solar cells but also applicable to near-infrared amplifiers due to their unique spectral characteristics.

Judd–Ofelt (J–O) theory is commonly applied to RE doped glasses to testify the spectroscopic and laser properties such as radiative transition probabilities, radiative lifetime, branching ratios of certain emitting levels of RE ions based on absorption spectrum. Detailed theoretical and calculation method have been well described in previous publications^{17,34–37}. Thus, only results for the Lead bismuth borate Pr³⁺ doped glass will be presented. The obtained Judd–Ofelt intensity parameters, Ω_λ ($\lambda = 2, 4$ and 6) for several host glasses containing Pr³⁺ ions are reported in Table 1. As it is known, the Ω_2 is related to the covalency of RE ions and ligand anions, which reflects the asymmetry of local environment around the RE ions. The covalency of Pr–O bond, in the studied glass, is stronger than those of zinc-bismuth-borate²⁹, lead-phosphate³⁰, oxyfluoride³¹, fluorotellurite³² and silicate³³ glasses, pointing therefore to stronger asymmetry around the RE ion. Ω_4 and Ω_6 are associated to the bulk properties like rigidity and viscosity of hosts.

The most intense absorption peak in the blue region is the result of the excitation of Pr³⁺ ions from ground state, 3H_4 to excited states, $^3P_j(^1I_6)$ ($j = 0, 1$ and 2), which contribute to NIR and visible emissions (see Fig. 3a, b). In the present work, upon 443 nm excitation, the Pr³⁺ ions are excited to 3P_2 level and non-radiative decay to 3P_0 and 1D_2 levels. Then, radiatively decay to lower levels of Pr³⁺ ions, exhibiting NIR and visible emissions of Pr³⁺ ions (see Fig. 3d). Subsequently, emission corresponding to the transition of Yb³⁺: $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission occurs in Pr³⁺/Yb³⁺ co-doped glasses. In order to feed the ions to Yb³⁺: $^2F_{5/2}$ level, there are two possible resonant energy transfer processes involved, ET1: (3P_0 (Pr³⁺) : $^2F_{7/2}$ (Yb³⁺)) \rightarrow (1G_4 (Pr³⁺) : $^2F_{5/2}$ (Yb³⁺)) and ET2: (3P_0 (Pr³⁺) \rightarrow 2 \times ($^2F_{7/2} \rightarrow ^2F_{5/2}$) (Yb³⁺)) (see Fig. 3d)^{38–40}. Most of previous studies point out that the ET1 is more efficient than that of the cooperative energy transfer (ET2).

| Glass | Ω_2 | Ω_4 | Ω_6 |
|-----------------------------------|------------|------------|------------|
| Lead bismuth borate | 1.40 | 0.30 | 1.26 |
| Zinc bismuth borate ²⁹ | 1.30 | 3.29 | 2.13 |
| Lead phosphate ³⁰ | 0.34 | 6.68 | 5.91 |
| Oxyfluoride ³¹ | 0.13 | 4.09 | 6.33 |
| Fluorotellurite ³² | 0.98 | 1.39 | 13.50 |
| Silicate ³³ | 0.71 | 1.33 | 5.15 |

Table 1. Judd–Ofelt intensity ($\Omega_\lambda \times 10^{-20}$ cm²) parameters of different Pr³⁺ doped glasses.

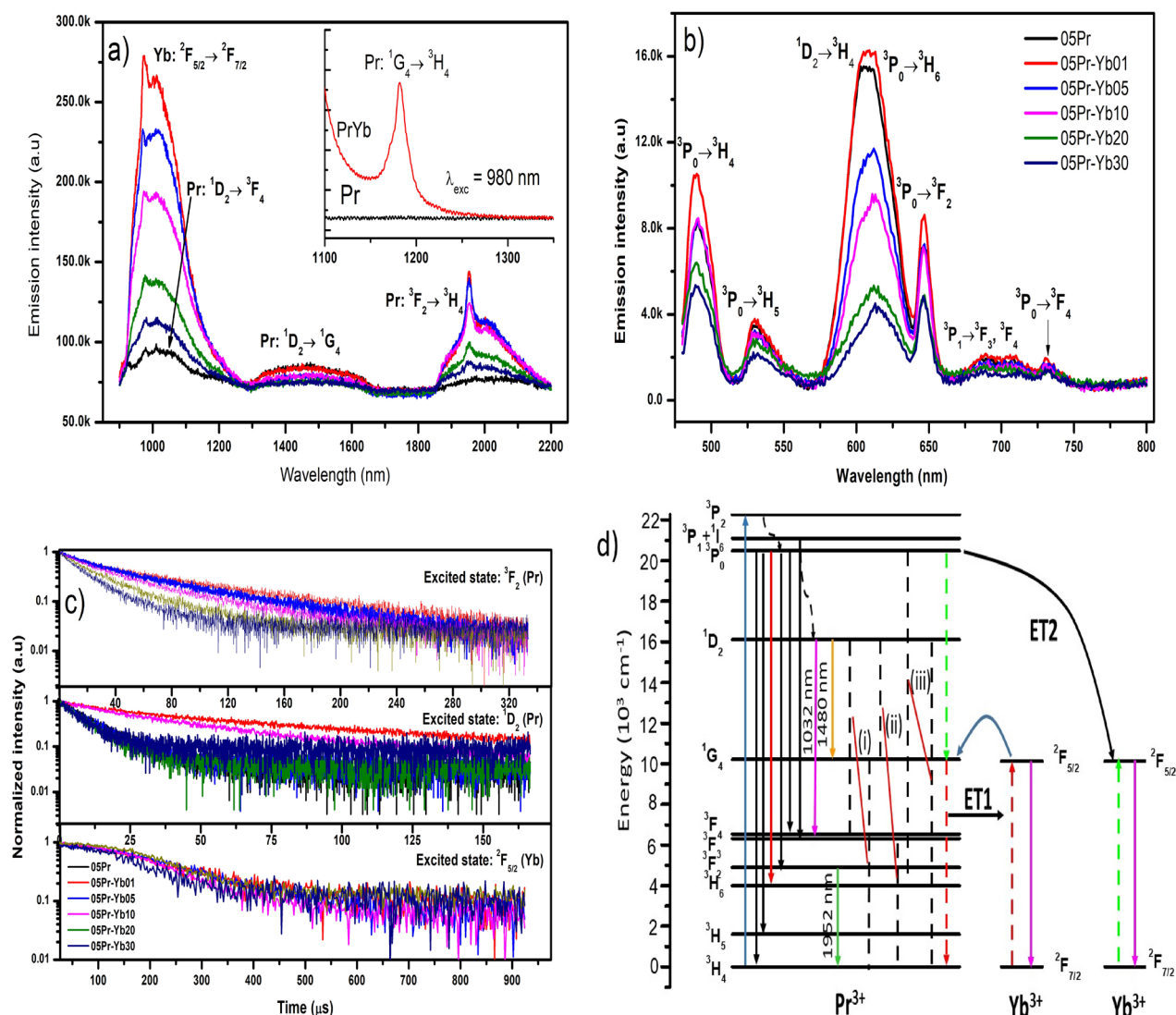


Figure 3. (a) NIR emission spectra upon 443 nm excitation and (b) visible emission spectra of glasses, (c) decay curves of excited levels of Pr³⁺ and Yb³⁺ ions, (d) schematic energy level diagram with possible energy transfer between Pr³⁺ and Yb³⁺ ions with cross-relaxation mechanisms. Inset of (a) shows NIR emission upon 980 nm excitation.

As can be seen in the luminescence spectra and energy matching condition of Pr³⁺, Yb³⁺ ions, upon 443 nm excitation, the emission around 900–1300 nm corresponds to the Yb³⁺: ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ (~ 980 (1010) nm) transition together with Pr³⁺: ${}^1D_2 \rightarrow {}^3F_4$ (~ 1035 nm) transition. The efficient NIR QC luminescence around 1.0 μ m monotonically decreases with increasing Yb³⁺ ions concentration due to cross-relaxation (CR) process, (${}^1D_2 \rightarrow {}^3F_4$): (${}^2F_{7/2} \rightarrow {}^2F_{5/2}$), which is predominantly responsible for the luminescence quenching by ions. The decrease of the lifetime of Yb³⁺: ${}^2F_{5/2}$ level (see Table 2) with increase of Yb³⁺ strongly supports the concentration quenching mechanism rather than back transfer of energy mechanism^{41,42}. De-excitation of Pr³⁺ ions to 1G_4 and ${}^3F_2 + {}^3H_6$ generates around 1480 nm and 1952 nm simultaneous emission. The ${}^1D_2 \rightarrow {}^1G_4$ (~ 1480 nm) emission is negligibly small and its lifetime decreases from 11.7 to 8.4 μ s due to CR process, (i) (${}^1D_2 \rightarrow {}^3F_{3,4}$): (${}^3H_4 \rightarrow {}^1G_4$) and (ii) (${}^1D_2 \rightarrow {}^1G_4$): (${}^3H_4 \rightarrow {}^3F_{3,4}$)⁴³. Similar experimental lifetime of 1D_2 level was obtained for gallo-germanate glass doped with 0.5 mol% Pr³⁺ ions (12 μ s)⁴³. It is worth to note that the multiphonon-relaxation rates from 3P_0 and 1D_2 are very small due to an insufficient number of phonons to bridge the energy gap between 3P_0 1D_2 (~ 3000 cm⁻¹) and 1D_2 1G_4 (~ 7000 cm⁻¹). Therefore, one can expect that the decrease visible emission intensity of Pr³⁺ via energy transfer followed by CR mechanisms, (ii) and (iii) (${}^3P_0 \rightarrow {}^3H_6$): (${}^3H_4 \rightarrow {}^1D_2$)⁴⁰.

In the present work, the visible emission intensity decreases with increase of Yb³⁺ ions concentration for a fixed concentration of Pr³⁺ at 0.5 mol%. Generally, energy transfer in a pair of ions occurs due to resonant energy levels between donor and acceptor ions, or through phonon assistance. Also, the average distance between Pr and Yb ions is greatly influenced by the concentration of Yb³⁺. Therefore, based on previous assertions, the decrease of visible emission in co-doped systems is likely to be carried out by the CR mechanisms (ii & iii, see Fig. 3d) when the average distance between Pr-Yb is shorter than a critical distance for an efficient energy transfer

| Glass doped RE ³⁺ ions | | Lifetime (τ) (μ s) | | | η_{ET} | η_{QE} |
|-----------------------------------|-------------------------|--------------------------------|-----------------------------|-----------------------------|-------------|-------------|
| Pr ³⁺ (mol%) | Yb ³⁺ (mol%) | ² F _{5/2} | ¹ D ₂ | ³ F ₂ | % | % |
| 0.5 | 0 | – | 11.7 | – | – | 100 |
| 0.5 | 0.1 | 195 | 11.6 | 72.7 | 1 | 101 |
| 0.5 | 0.5 | 210 | 10.9 | 57.1 | 7 | 107 |
| 0.5 | 1.0 | 156 | 10.3 | 42.5 | 12 | 112 |
| 0.5 | 2.0 | 144 | 9.3 | 29.9 | 21 | 121 |
| 0.5 | 3.0 | 134 | 8.4 | 18.5 | 28 | 128 |

Table 2. Lifetimes of Yb³⁺: ²F_{5/2} and Pr³⁺: ¹D₂ & ³F₂ excited levels as a function of Yb³⁺ in glasses^{38,39}.

(~ 10 Å)⁴⁴. The remarkable decrease of visible emission intensity maxima of ¹D₂ → ³H₄ (~ 604 nm) with respect to ³P₀ → ³H₆ emission (~ 612 nm), is due to the competition between the above mentioned CR mechanisms. According to literature⁴⁵, the expected experimental lifetime for ¹D₂ → ³H₄ emission is equal to the ¹D₂ → ¹G₄ (~ 1480 nm) emission lifetime values (see Table 2). Moreover, the energy transfer efficiency (η_{ET}) between Pr³⁺–Yb³⁺^{46–48} and total quantum efficiency (η_{QE}) of ions excited to ³P_J levels are important parameters and can be expressed as follows,

$$\eta_{ET} = 1 - \frac{\tau_{(Pr,Yb)}}{\tau_{Pr}}, \quad (1)$$

$$\eta_{QE} = \eta_{Pr}(1 - \eta_{ET}) + 2\eta_{ET}, \quad (2)$$

where, $\tau_{(Pr,Yb)}$ and τ_{Pr} (11.7 μ s) are the average lifetimes with and without Yb³⁺ ions, respectively, and η_{Pr} is set to be 1^{38,39}. Table 2 reports the energy transfer efficiencies for the ¹D₂ → ¹G₄ transition. The η_{ET} is increased from 1 % to 28 %, and η_{QE} is increased from 100 to 128 % with increasing Yb³⁺ ions. The η_{QE} is an indicative of the ratio increase of emitted photons compared to the absorbed photons in function of the Yb³⁺ concentration.

Figure 3a also shows NIR luminescence around 2.0 μ m in 1850–2200 nm wavelength region, attributed to the Pr³⁺: ³F₂ → ³H₄ transition upon 443 nm excitation. We assume that the ³F₂ and ³H₆ multiplets are populated from ¹G₄ levels. As can be seen in Fig. 2a, the ³H₄ → ¹G₄ absorption band has low intensity and quite low absorption cross-section which indicates that populating ¹G₄ level by direct excitation is not efficient. Therefore, sensitizing Pr³⁺ with Yb³⁺ is more efficient to populate ¹G₄ level via the emission of Yb³⁺: ²F_{5/2} → ²F_{7/2} which nicely overlaps the absorption of Pr³⁺: ³H₄ → ¹G₄, indicating that the resonant energy transfer may occur as, (²F_{5/2}(Yb³⁺): ³H₄(Pr³⁺)) → (²F_{7/2}(Yb³⁺): ¹G₄(Pr³⁺)). Considering the efficient QC in between Pr³⁺ and Yb³⁺ with increasing Yb³⁺ ions, and resonant transfer of energy, the emission of ¹G₄ level should vanish. However, we could not neglect the back transfer of energy from Yb³⁺ which could become more and more efficient inducing an increase of ¹G₄ population. In singly Pr³⁺ doped glass, we could not detect emission from ¹G₄ level, but the Pr³⁺/Yb³⁺ co-doped glass exhibit an emission around 1182 nm which corresponds to Pr³⁺: ¹G₄ → ³H₄ transition (see inset of Fig. 3a). Therefore, we believe that the back transfer energy greatly contribute for the observed 2.0 μ m emission in co-doped samples. Unfortunately, the emission intensity of Pr³⁺ (³F₂ → ³H₄) might transfer energy to OH[−] groups. The observed fluorescence decay curves for the ³F₂ excited level are well fitted with single exponential function (Fig. 3c), indicating that there is no significant nonlinear energy transfer between Pr³⁺ ions other than transfer of energy to OH quenching centers. This is confirmed by the decrease lifetime of the excited ³F₂ level and the measured lifetime written as follows⁴⁹,

$$\frac{1}{\tau_m} = A_{rad} + W_{mpr} + W_{OH}, \quad (3)$$

where A_{rad} is the radiative decay rate, which is equal to the reciprocal of the decay rate in the absence of OH groups ($1/\tau_0$). W_{mpr} is the multiphonon decay rate, and W_{OH} is the energy transfer rate between Pr³⁺ and OH[−].

The gain performance at 1952 nm of the optimized glass can be evaluated through determination of the stimulated emission cross-section¹²,

$$\sigma_e(\lambda) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff} \tau_m} \quad (4)$$

where λ_p is the emission peak wavelength, c is velocity of light, n is refractive index, $\Delta\lambda_{eff}$ is the effective linewidth and τ_m is the measured lifetime. Table 3 presents important spectroscopic parameters of Pr³⁺ doped for several glasses. The σ_e near 2.0 μ m is one order (10^{-19}) higher than those of RE³⁺ doped tellurite⁵⁰, germanate¹³, and silicate⁵¹ glasses. As it is known, materials which present large stimulated emission cross-section exhibit low threshold and high gain laser operation. In our case, the σ_e and figure of merit ($\sigma_e \times \tau_m$) are relatively higher than the reported glasses in Table 3, suggesting that 0.5Pr³⁺/0.1Yb³⁺ codoped PbO–Bi₂O₃–B₂O₃ glass is a promising material for NIR broadband amplifiers. The wavelength dependent gain cross-section can be obtained as a function of population inversion and is written as¹², $G(\lambda) = P\sigma_e(\lambda) - (1-P)\sigma_a(\lambda)$, where P is the population inversion of Pr³⁺ ions, absorption and emission cross-sections $\sigma_a(\lambda)$ & $\sigma_e(\lambda)$ derived from Beer-Lambert and

| Glass | σ_e (cm ²) | τ_m (s) | $\sigma_e \times \tau_m$ (cm ² s) |
|-----------------------------------|-------------------------------|------------------------|--|
| Lead bismuth borate (0.5Pr/0.1Yb) | 6.79×10^{-19} | 72.71×10^{-6} | 4.94×10^{-23} |
| Tellurite (Ho/Tm) ⁵⁰ | 9.33×10^{-20} | 3.29×10^{-3} | 3.07×10^{-23} |
| Germanate (Yb/Tm) ¹³ | 6.90×10^{-20} | 1.04×10^{-3} | 0.72×10^{-23} |
| Silicate (Tm) ⁵¹ | 3.60×10^{-20} | 7.91×10^{-3} | 2.84×10^{-23} |

Table 3. Emission properties of near 2.0 μm in RE³⁺ doped glasses.

McCumber equations¹². Figure 4 shows the gain cross-section of Pr³⁺: $^3F_2 \rightarrow ^3H_4$ transition as a function of population inversion (0–1) varied with an increment of 0.1. It can be seen that the gain becomes positive at $P = 0.3$ in the range of 2075–2300 nm, which means a low pump threshold of Pr³⁺: $^3F_2 \rightarrow ^3H_4$ laser operation. Also, the observed positive gain band becomes longer with the increase of P which is a characteristic of a quasi-three level system⁵¹.

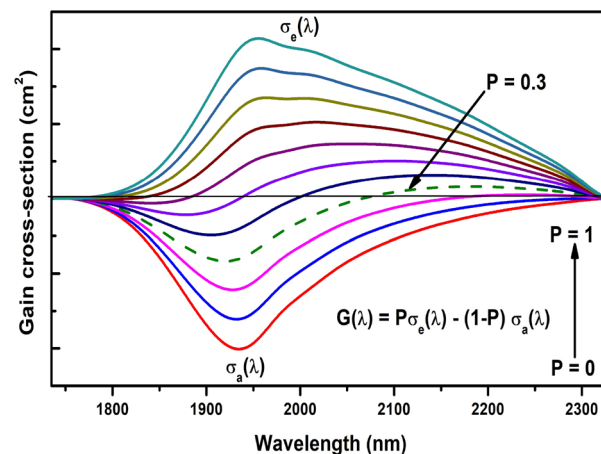
Conclusions

In summary, Pr³⁺/Yb³⁺ codoped PbO – Bi₂O₃ – B₂O₃ glasses were successfully prepared by melt-quenching technique. The structural, thermal and near-infrared emission properties are investigated. From Raman and DSC results, we found an increase in glass transition temperature, (T_g), with an increase of Yb³⁺ ions concentration which reflects the enhancement of rigidity of the glasses, decrease of Bi³⁺ cations in [BiO₃] and [BiO₆] units, and decrease of B–O bonds by the formation of B–O–B linkages in pyro-borate structural units. Concerning emissions, we found near-infrared emissions around 980, 1010, 1480 and 1952 nm in the wavelength range 900–2200 nm under 443 nm excitation. The observed concentration quenching is discussed in detail. Quantum effectiveness of the glasses, η_{QE} , has increased from 100 to 128.2% with increasing of Yb³⁺ content which may be used to mimic the solar spectrum aiming its use to enhance the efficiency of c-Si solar cells. The optimized glass (0.5Pr³⁺/0.1Yb³⁺) possess relatively large $\sim 2.0 \mu\text{m}$ ($^3F_2 \rightarrow ^3H_4$) emission cross-section and high figure of merit implying that this glass can be a promising candidate for $\sim 2.0 \mu\text{m}$ Pr³⁺ laser operation with low pump threshold.

Methods

Pr³⁺/Yb³⁺ codoped lead-bismuth-borate glasses were prepared by melt-quenching method. The glasses have molar composition of $(59.5 - x)\text{B}_2\text{O}_3 + 25\text{Bi}_2\text{O}_3 + 15\text{PbO} + 0.5\text{Pr}_6\text{O}_{11} + x\text{Yb}_2\text{O}_3$ ($x = 0, 0.1, 0.5, 1.0, 2.0$ and 3.0). Analytical grade reagents of H_3BO_3 , Bi_2O_3 , PbO , Pr_6O_{11} and Yb_2O_3 were used as raw materials, from which nominal batches of 10 g were prepared and mixed in an agate mortar. Then, the mixture was melted in porcelain crucible at 1050 °C in air for 1 h 30 min and melt was poured into stainless steel moulds. The obtained glass samples were cut and polished for optical characterization.

Differential Scanning Calorimetry was performed with NETZSCH DSC 404F3 with heating rate of 10 °C/min in order to determine the glass transition (T_g) and crystallization temperature (T_x) of the glass samples. Raman spectra were recorded with a Renishaw inVia spectrometer coupled with a Leica DM2700 microscope with 633 nm laser excitation. Optical absorption spectra of the glass were recorded on UV-2500 (SHIMADZU) and NIR (BRUKER MPA—Multi Purpose Analyzer) spectrophotometers. Luminescence measurements were performed on Florolog3-iHR HORIBA fluorescence spectrometer upon 443 nm excitation. Density of the glass samples were estimated with distilled water as immersion liquid by Archimedes' method. All the measurements were conducted at room temperature.

**Figure 4.** Gain cross-section near 2.0 μm emission of Pr³⁺.

Data availability

The data sets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Competing interests

The authors declare no competing interests.

Additional information

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