

Research Article

Energy Transfer Kinetics and Luminescence in Nd³⁺/Yb³⁺Co-Doped Lead-Borate Glasses at 800 nm Excitation

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Abstract

Nd³⁺ and Nd³⁺/Yb³⁺ ion-doped lead-borate glasses were created. For the thermal studies of sample such as glass transition temperature, crystallization temperature and, melting temperature T_m, differential scanning calorimetry (DSC) is done. The X-ray diffraction is used to justify the glassy nature of the samples. UV-VIS-IR of the prepared samples is carried for the studies of absorption bands available in Nd³⁺ and Nd³⁺/Yb³⁺ ion-doped lead-borate glasses. For the studies of fluorescence spectra and energy transfer mechanism the samples were excited at 800nm and spectra is recorded. The Nd³⁺ glasses exhibited strong NIR emission at 1mol% concentration at 903, 1068, and 1348 nm upon pumping at 800 nm. These transitions were labelled as ⁴F_{3/2}→⁴I_{9/2}, ⁴F_{3/2}→⁴I_{11/2}, and ⁴F_{3/2}→⁴I_{13/2}. Interpretation is given to the effects of multiphonon, cross-relaxation, and OH- group on Nd³⁺ emission that causes photoluminescence quenching above 1.0mol% Nd³⁺. Through the co-doping of Nd³⁺ ion (1mol%) and Yb³⁺ ion (1mol%) concentrations, the sensitising impact of Nd³⁺ emission on Yb³⁺ luminescence is examined. The significant spectrum of Yb³⁺ absorption and Nd³⁺ emission, photoluminescence characteristics, has supported the likelihood of energy-transfer (ET) between these ions. The findings show that the Neodymium ion (⁴F_{3/2})→ytterbium ion (⁴F_{5/2}) energy-transfer process is of a non-radiative type controlled by phonon-assisted electric dipole-dipole interaction.

Keywords

Lead-Borate Glasses, Multiphonon Relaxation, Cross Relaxation

1. Introduction

Research on the optical characteristics of solid-state materials containing single and dual combinations of di- and trivalent lanthanide ions has made it possible to gain a thorough understanding of the energy transfer process. Novel pumping strategies were developed in tandem through the evolution of laser diodes (LDs) in solid-state lasers to provide improved

lasing process at lower threshold frequency, hence fostering novel opto-electronic features. Neodymium (Nd³⁺) and ytterbium (Yb³⁺) are two opposing ions among the rare earths. Since the development of Nd³⁺-based optical lasers, the Nd³⁺ ion with ⁴F₃ configuration which has a ⁷F₀ ground and a ⁵D₀ lower excited state has been the most studied active centers in

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relation to lanthanides doped lasers, regardless of the host's crystalline or amorphous nature [1-3].

Neodymium (Nd^{3+}) lasers have a four-level system that may operate in a continuous or pulsed mode. For instance, Nd^{3+} : YAG crystals exhibit a strong and focused emission at/around $1\mu\text{m}$ ($1.064\mu\text{m}$), whereas glasses containing Nd^{3+} exhibit emission between 1.054 and $1.056\mu\text{m}$ [4, 5]. Additionally, it displays near-ultra violet laser line at 514.5 nm and near-NIR laser transitions at $0.92\mu\text{m}$ and $1.34\mu\text{m}$ [6]. Furthermore, Nd^{3+} ions may efficiently absorb solar energy in the 582 nm absorption band at ($^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2} + ^2\text{G}_{7/2}$). Due of undesirable effects similar to multi-phonon with cross-relaxation, Nd^{3+} is more susceptible to luminescence quenching when there are more exciting levels with greater absorption probability. But the Yb^{3+} ion, which has a special pumping level scheme made up of two manifolds $^2\text{F}_{5/2}$ for the excited state and $^2\text{F}_{7/2}$ for the ground state is also a possible laser active ion. In addition to NIR tunability and mode-locking operation, non-radiative losses such as OH^- group effects, cross-relaxation, and multi-phonon relaxations have significantly less of an impact on the Yb^{3+} ion. Longer lived excited states also have higher energy storage efficiency [7, 8]. For up-and down-conversion experiments, Neodymium ions and ytterbium ions are commonly co-doped as sensitizers to various near-infrared emitting activators such as praseodymium, erbium, holmium, and thulium ions. Neodymium and ytterbium ions were supposed to co-dope in the NABFBS host glass based on this situation. The integration of Neodymium ions and ytterbium ions into a host matrix with low phonon strength can open up new potential for the growth of ultra short pulsed lasers with superior efficiency and better lasing properties for advanced applications. Effective solar energy incorporation for tunable lasers and solar concentrators is ensured by the non-radiative energy transfer from Nd^{3+} to Yb^{3+} , which emits light at $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ brightness levels, fitting well with the silicon solar cell energy-gap (9182cm^{-1}). Pr^{3+} -doped fibre amplifiers may also be pumped using the Neodymium/ytterbium ions coupled system (Nd/Yb : YAG laser) at or around 1330 nm ($^1\text{G}_4 \rightarrow ^3\text{H}_5$) [9]. The Forster-Dexter theory states that the host matrix doped with lanthanide ion(s) that show small emission intensities because of deprived excited energy absorption or a reduce in luminescence intensity because of absorption quenching from non-radiative relaxations is meant to dope in addition to another lanthanide ion (called a donor or sensitizer) to the original doped ion (called an activator or acceptor). Luminescence characteristics are increased when the excitation energy is first absorbed by the sensitizer/donor and then transferred to the activator/acceptor through a non-radiative energy transfer mechanism or by releasing radiation that are then reabsorbed by the acceptor centers [10, 11]. Energy transfer between optically active ions improves the properties of photoluminescence, such as absorbance, luminescence intensity, life-times, and quantum efficiencies.

The host glass substrate powered by luminescent active

(lanthanide metal) ions for laser and display operations should be a crucial component to enhance optical and luminescence-related features.

In order to address this, we suggested creating borosilicate glass based on oxy fluoride that contains bismuth oxide, aluminum, and sodium oxide as modifiers and intermediates in the glass matrix. A special and unusual benefit exists for host glasses that combine components of fluoride and oxide over those that just contain fluoride or oxide. While the low-phonon energy fluorides lower non-radiative decay losses and boost the rare earths' quantum efficiency, the oxides offer mechanical strength, chemical resistance, and thermal stability.

Lead borate glasses exhibit increased optical non-linearity as a result of Pb^{2+} ions in glass matrices with a high polarizability [12, 13]. Such substances are appealing [13] for use in triggered Raman amplifiers, waveguides, and other optical switches.

Here, we primarily focus on examining the energy-transfer mechanism that occur while co-doping neodymium ions and ytterbium ions in a lead borate glass matrix. Based on optical and luminescence patterns, the Nd^{3+} ion concentration was first optimized in this technique to $1\text{mol}\%$. Afterwards, Yb^{3+} was co-doped in various concentrations with the glass that had an optimized concentration of $1\text{mol}\%$ Nd^{3+} .

2. Experimental Methods (Glass Sample Preparation)

The glass system of following batch composition

1. $60\text{B}_2\text{O}_3$ - 30PbO - $10\text{Na}_2\text{O}$ (reference glass)-PBN

2. 59% B_2O_3 - 30% PbO - 10% Na_2O - 1.0% Nd_2O_3 }-PBN

3.

58% B_2O_3 - 30% PbO - 10% Na_2O - 1.0% Nd_2O_3 - 1.0% Yb_2O_3 -PBN

NY were prepared by employing the classical melt-quench method. Reagent-grade chemicals B_2O_3 , PbO , Na_2O , Yb_2O_3 and Nd_2O_3 of Otto Chemie Pvt Ltd, were used. Separately weighed in 12g batch each and mixed thoroughly and powdered finely with agate mortar and pestle in open atmosphere. The precursor chemicals were ground until a homogeneous mix was obtained. The finely ground mixture, each batch weighing 12g is separately taken in an alumina crucible covered with the lid and heated in an electric muffle furnace for about 80 minutes at 910°C . To guarantee homogeneity, the mixture is physically agitated until a liquid without bubbles forms. Subsequently, the melts were poured into stainless steel pellet moulds to be cooled. In order to eliminate internal thermal stress, glass samples that had been quenched and measured about 0.8 cm in diameter and 0.3 cm in thickness were annealed for two hours at 350°C , the glass transition temperature. Ultimately, these glass samples were collected for further analysis.

3. Characterization

3.1. X-Ray Diffraction Spectra

X-Ray Diffractogram for the undoped and doped specimens were carried on a Rigaku Smart Lab 9kW x-ray diffractometer, plot obtained (Figure 1) is quit flat else a wide hump near 28 °, implies the the samples are glassy in nature.

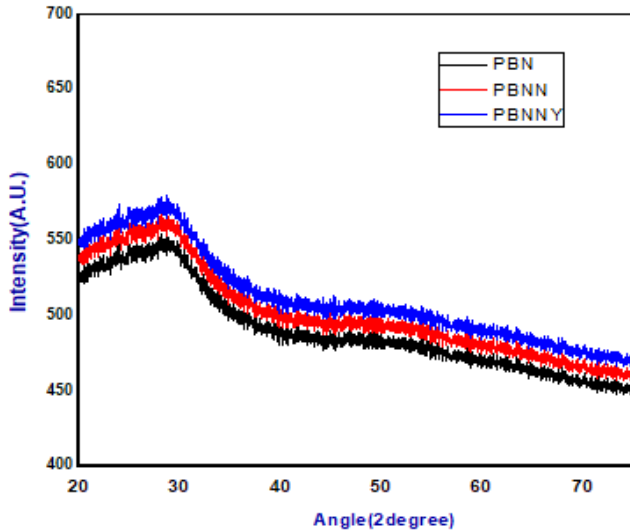


Figure 1. X-Ray diffraction plots of PBN, PBNN and PBNNY glasses.

3.2. Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) measurements were simultaneously carried out by TA instruments, USA, Q10) at a heating rate of 10 °C/min, the DSC plots were carried in r the temperature range 100 °C - 550 °C as shown in figure 2. For the prepared samples glass transition temperature T_g is observed near of 330 °C, crystallization temperature

T_c near 370 °C and, Melting temperature T_m were found around 450 °C.

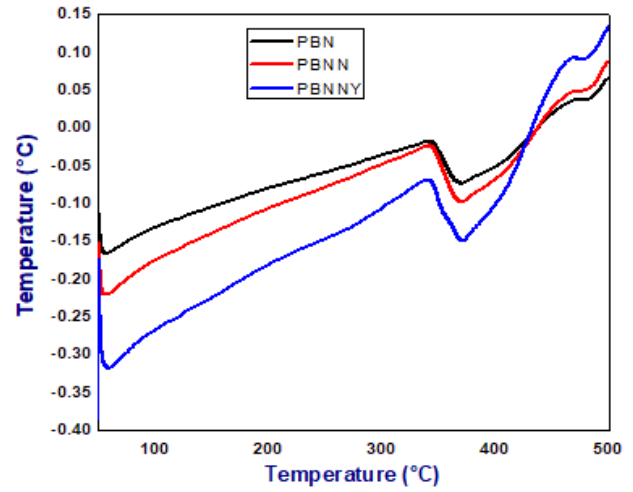
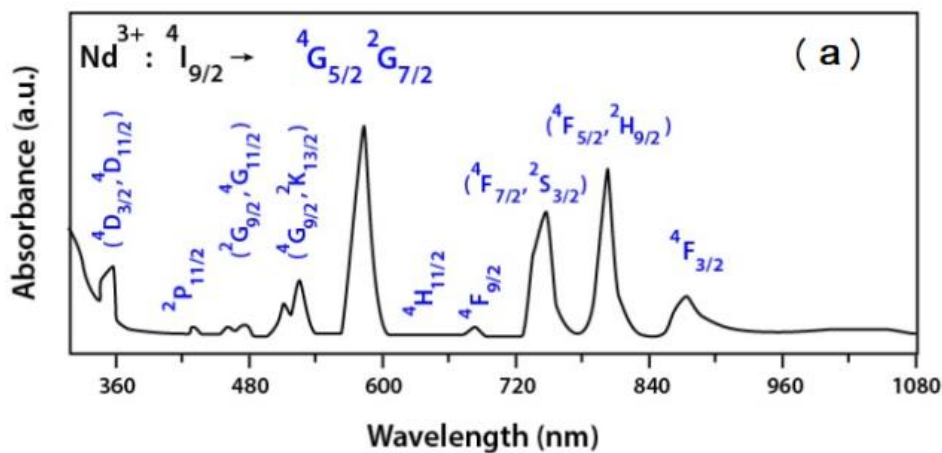


Figure 2. DSC plots of PBN, PBNN and PBNNY glasses.

4. Optical Analysis

4.1. Absorption Spectra

The absorption spectra of neodymium ions doped alone and in combination with ytterbium ions doped, PBNN and PBNNY glasses are shown in Figure 3(a) and Figure 3(b) correspondingly. A sequence of bands ranging from the lower lying $^4I_{9/2}$ state to $^4D_{3/2,11/2}$ (362 nm), $^2P_{1/2}$ (430 nm), $^2G_{9/2}$, $^4G_{11/2}$ (470 nm), $^4K_{13/2}$ (510 nm), $^4G_{9/2}$ (524 nm), $^4G_{5/2}$, $^2G_{7/2}$ (582 nm), $^4H_{11/2}$ (624 nm), $^4F_{9/2}$ (680 nm), $^4F_{7/2}$, $^4S_{3/2}$ (746 nm), $^4F_{5/2}$, $^4H_{9/2}$ (803 nm), $^4F_{3/2}$ (875 nm), and $^4I_{15/2}$ (1720 nm) were visible in the Nd^{3+} absorption spectrum. Nd^{3+}/Yb^{3+} co-doped glass's absorption spectra revealed a distinct band at 980 nm that was linked to the $Yb^{3+}: ^2F_{7/2} \rightarrow ^2F_{5/2}$ transition in addition to the Nd^{3+} absorption bands.



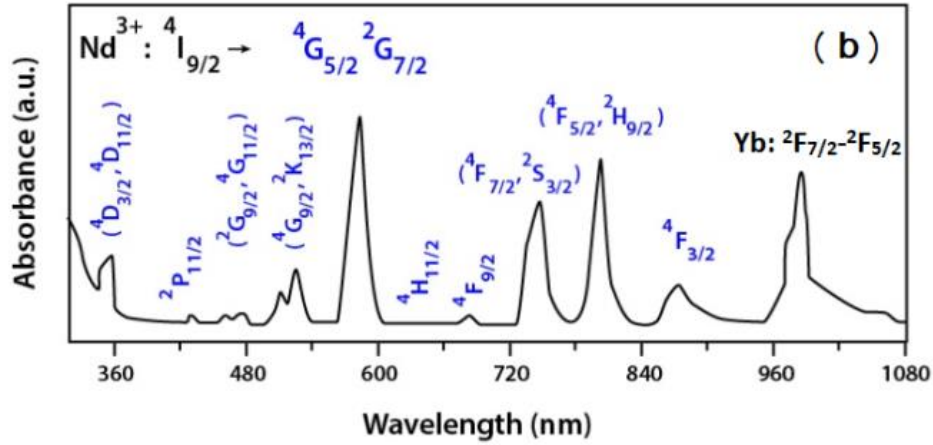


Figure 3. (a) Absorption spectra of PBNN glass. (b) Absorption spectra of PBNNY glass.

4.2. Fluorescence Spectra and Energy Transfer Mechanism

Figure 4 illustrate how, when pumped to 800 nm, the normal state Nd^{3+} ions absorb a photon to the $^4\text{F}_{5/2}$ and $^2\text{H}_{9/2}$ levels. They then relax to the $^4\text{F}_{3/2}$ level by a non-emission relaxation

mechanism, and luminescence starts at this $^4\text{F}_{3/2}$ level. The $^2\text{F}_{7/2}$ to $^2\text{F}_{5/2}$ emission of Yb^{3+} in $\text{Nd}^{3+}/\text{Yb}^{3+}$ PBNN and PBNNY glasses is caused by two effective $\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$ energy transfer processes, which may be divided into two main forms: ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$) and ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$). Ultimately, the emission at 1020 nm is caused by the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition [7].

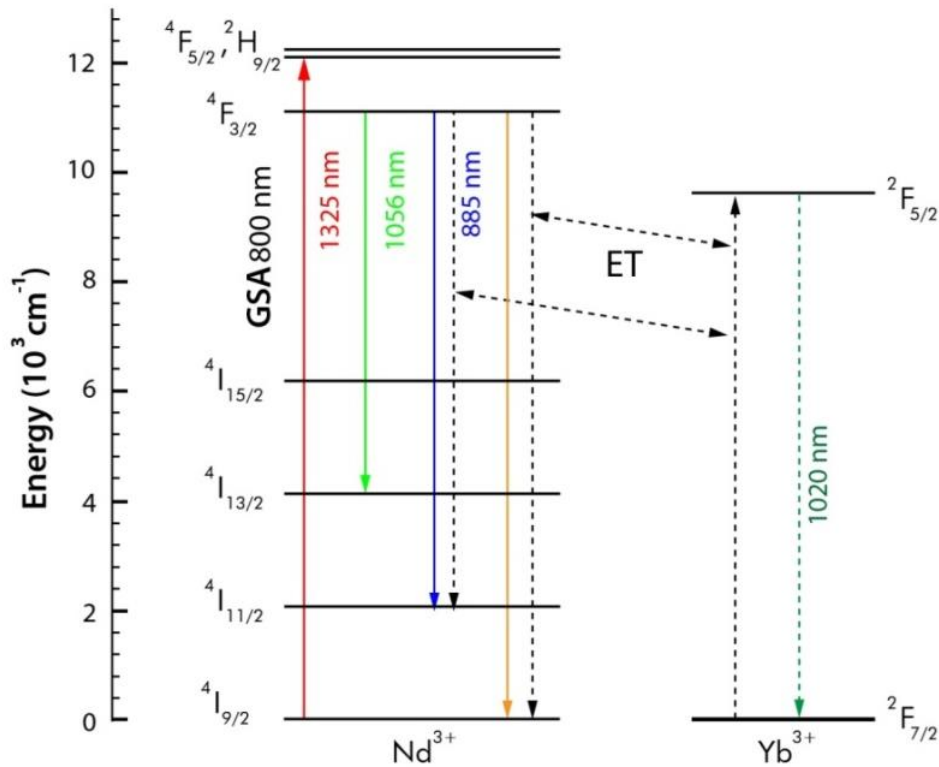


Figure 4. Fluorescence mechanism for Nd^{3+} and Yb^{3+} at 800 nm excitation in PBNN and PBNNY glasses.

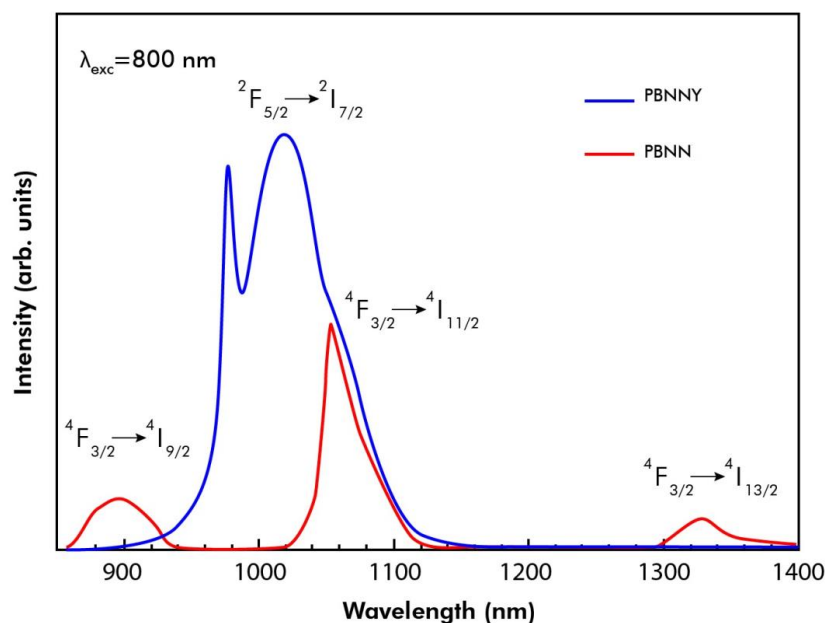


Figure 5. Luminescence Spectra of PBNN and PBNNY glasses at 800 nm excitation.

Luminescence spectra of lead-borate glasses doped with 1mol% Nd^{3+} and co-doped with 1mol% Nd^{3+} 1mol% Yb^{3+} under 800nm pumping are displayed in Figure 5. Three primary emission spectra at 885nm, 1056nm, and 1325nm are caused by the Nd^{3+} ion's $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}$ transitions. Under a laser stimulation at 800 nm, the typical near-infrared emission $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition of Yb^{3+} with peaks at 980 and 1020 nm is detected in the Neodymium/Ytterbium ions co-doped lead-borate glasses.

5. Conclusions

Conventional melt-quench method is used to create the Neodymium/Ytterbium ions co-doped lead-borate glasses. It is possible to acquire the spectroscopic characteristics of the samples pumped by 800 nm LD. This work describes the mechanism of energy transfer from Neodymium to Ytterbium ions and obtains a large energy transfer microparameter and high transfer efficiency between Neodymium and Ytterbium ions. According to the current research, glass co-doped at 1020 nm with 1.0 mol% Nd_2O_3 and 1.0 mol% Yb_2O_3 should be a great choice for Yb^{3+} fibre laser systems that use Nd^{3+} as a multiple pump guide source.

Abbreviations

ET	Energy-Transfer
UV-VIS-IR	Ultraviolet-Visible-Infrared

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Conflicts of Interest

The authors declare no conflicts of interest.

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