Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 115 (2013) 297–304

Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

NIR fluorescence studies of neodymium ions doped sodium fluoroborate glasses for 1.06 μm laser applications

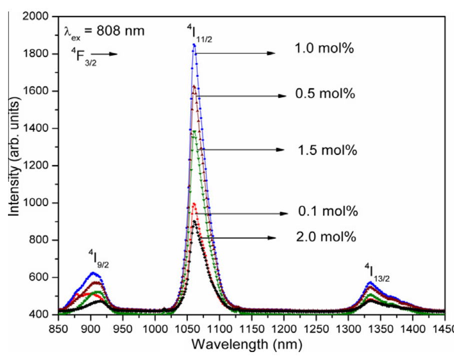
C. Madhukar Reddy [a], N. Vijaya [a], B. Deva Prasad Raju [b,a,*]

[a] Department of Physics, Sri Venkateswara University, Tirupati 517 502, India
[b] Department of Future Studies, Sri Venkateswara University, Tirupati 517 502, India

HIGHLIGHTS

- In this study we prepared LCZSFB glasses doped with Nd^{3+} ions.
- Judd–Ofelt theory is used to analyze absorption and emission spectra.
- Various radiative and fluorescence properties are calculated and compared.
- LCZSFB glasses have found favorable lasing action at 1.06 μm.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 April 2013
Received in revised form 3 June 2013
Accepted 5 June 2013
Available online 24 June 2013

Keywords:
Glasses
Neodymium
Oscillator strength
Branching ratio
Fluorescence
Lifetime

ABSTRACT

The concentration dependent luminescence properties of Nd^{3+} ions doped lead calcium zinc sodium fluoroborate (LCZSFB) glasses were prepared via a melt quenching technique and reported through optical absorption, NIR luminescence and lifetime measurements. The optical transition properties of Nd^{3+} ions have been analyzed using Judd–Ofelt theory. The present glasses have high stimulated emission cross – sections, entail that they have high potential laser applications. The decay curves of all the glasses show single exponential behavior. The discrepancy between the experimental and calculated lifetimes of emitting level was ascribed to energy transfer through cross-relaxation. The estimated values of radiative and saturation intensity of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition indicates the favorable lasing action at 1.06 μm.

Introduction

Glass finds increasingly wide applications in modern science and technology i.e., particularly in the rapid developments in information technology due to its optical properties. The incorporation of rare earth (RE) ions into glasses brought much attention to search for new laser areas to extend the application of laser materials to new spectral ranges. Due to prominent features of RE ions such as many excited levels suitable for optical pumping, sharp absorption and emission bands from ultra violet (UV) to infrared (IR) spectral range, and longer lifetimes, have been well suited for the optical devises including solid state lasers, fiber amplifiers, infrared to visible up-converters, phosphors, field emission displays, biosensors, solar cells, etc. for variety of applications [1–3]. Recently there has been a great deal of interest in the near infrared (NIR) lasing glasses to assist a rapid development in the field of photonics and photonic materials suitable for optical device fabrication and for the development of telecommunication

* Corresponding author at: Department of Future Studies, Sri Venkateswara University, Tirupati 517 502, India. Tel.: +91 94402 81769.
E-mail address: drdevaprasadraju@gmail.com (B. Deva Prasad Raju).

1386-1425/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2013.06.029

industry [4,5]. With the fast development of diode-pumped solid state laser technology, research on more efficient new laser materials has gained the importance [6]. In this direction, solid state lasers operating in the NIR region have important applications in the fields such as optical communication, radar and medical instrumentation [7]. The materials which have good laser performance characteristics, i.e., high laser gain, high energy storage capacity and low optical losses, are used as a laser active medium. Moreover, it is well recognized that the gain and the energy storage capacity are strongly affected by the stimulated emission cross section, fluorescence lifetime and coupling efficiency of the pump energy [8,9].

Over the past decade much attention has been devoted to develop the Nd^{3+} ions doped different glass matrices. Moreover, optical properties of Nd^{3+} ions in lead borate glasses with different chemical compositions are well documented in the literature and it is observed that the small modification of lead borate glass matrix affect significantly on spectroscopic and laser properties of Nd^{3+} ions. For instance, Saisudha and Ramakrishna [10,11] have reported the effect of host glass on the optical absorption properties of Nd^{3+}, Sm^{3+} and Dy^{3+} in lead borate glasses suitable for laser applications and also examined the fluorescence properties of Nd^{3+} in lead borate and bismuth borate glasses with large stimulated emission cross section. Karthikeyan and Mohan [12] have studied the structural, optical and glass transition studies on Nd^{3+}-doped lead bismuth borate glasses. Courrol et al. [13,14] have reported the spectroscopic properties of Nd^{3+}-doped lead fluoroborate glasses and also studied the upconversion losses in Nd^{3+} doped lead fluoroborate glasses. Pisarska et al. [15,16] have reported the spectroscopic investigations of Nd^{3+} ions in B_2O_3–PbO–Al_2O_3–WO_3 glasses concluding that the quantum efficiency of $^4F_{3/2}$ excited state of Nd^{3+} ions in oxide lead borate based glass system is larger in comparison to traditional borate glasses and also examined the Nd-doped oxyfluoroborate glasses and glass ceramics for NIR laser applications concluding that the addition of fluoride components to the oxide glass matrices influence significantly on elongation in luminescence lifetime and other spectroscopic parameters of Nd^{3+} ions. Mohan et al. [17] have reported spectroscopic investigations of Nd^{3+} doped fluoro and chloro borate glasses. Petrova et al. [18] have reported the lead borate oxyfluoride glasses doped with Nd^{3+} ions and transparent glass crystal materials based on them. Though spectroscopic characterizations have been significantly studied by the alteration of compositions to improve the performance of laser hosts, still there is a great demand for novel host materials with high laser gain coefficient.

In the process of searching of possible glass compositions, lead containing calcium zinc sodium fluoroborate (LCZSFB) glass system has been chosen for the present investigation. The LCZSFB glass result from the combination of network forming oxides PbO and B_2O_3 together with the network modifiers CaO, ZnO, and NaF. The interest in the present host matrix is due to the individual properties of its ingredients. B_2O_3 is a well known glass former and is the major component in the glass composition has a capability of accepting higher concentration of dopant ions [19]. Also borate glasses have been found to be suitable optical materials with high transparency, low melting point, high thermal stability and good RE ion solubility. Moreover, borate glasses are significant hosts for RE ions because of their better mechanical properties, but at the same time the RE ion emissions are strongly reduced due to their high phonon (lattice vibrations) energy ($\sim$1300 cm^{-1}). It has been shown that heavy metal oxide (HMO) such as PbO based glasses are very attractive hosts for RE ions with useful characteristics for photonics and optoelectronics applications, and the addition of PbO to borate results in an increased refractive index, thermal stability and decrease in phonon energy of the host. In consequence, larger quantum efficiencies of RE excited states were expected due to smaller multi phonon decay rates and large radiative transition probabilities. Quenching of luminescence intensity is one of the major problems in selecting the laser host material. Normally, if neodymium oxide is immiscible in glass host, forms aggregates or clusters in which cross-relaxation can give rise to non-radiative de-excitation of neodymium, resulting in very short lifetimes and fluorescence quenching. Recently, Sundara Rao et al. [20] studied the de-clustering influence of aluminum ions on the emission features of Nd^{3+} ions in PbO–SiO_2 glasses. The addition of alkali/alkaline earth oxide/fluoride converts the boron coordination and the structural groups from one to another depending on the type and concentration of the alkali/alkaline earth oxide/fluoride. Among the oxide and mixed oxy-fluoride glass compositions lead borate glasses doped with RE ions seem to be very attractive system for applications in laser technology [21].

We believed that it is interesting to extend the spectroscopic investigations to the Nd^{3+} ion, which is considered as one of the most important dopant for laser applications in the NIR region at around 1.06 μm. Glasses activated with RE ions, emitting in NIR region are of current interest because of their potential as laser host materials and optical fiber amplifiers for use in telecommunications [22]. Among all the RE ions, Nd^{3+} is one of the most important RE ions for obtaining laser emission in the NIR region. The suitability of this ion in producing strong infrared fluorescence radiation makes it as a possible candidate in high power laser applications. The technological interest in glasses containing Nd^{3+} suddenly arose due to the demonstration of laser action in Nd^{3+}-doped glasses by Snitzer in 1961 [23]. Even though several authors [4–19] studied the structural properties of borate glasses and the optical properties of Nd^{3+} ions, an attempt has been made in the present investigation to study the structural, thermal and concentration dependent optical properties of Nd^{3+}-doped LCZSFB glasses due to above mentioned advantages and applications.

Experimental methods

A series of LCZSFB glasses doped with different concentrations of Nd_2O_3 were prepared by the melt quenching method with the molar composition 20PbO + 5CaO + 5ZnO + 10NaF + $(60 - x)$ B_2O_3 + xNd_2O_3, (where x = 0.1, 0.5, 1.0, 1.5 and 2.0 mol%) using the reagent grade chemicals Pb_3O_4, $CaCO_3$, ZnO, NaF, H_3BO_3 and Nd_2O_3 as starting materials. The stoichiometric compositions of these raw materials were mixed thoroughly in an agate mortar and melted in a programmable electric furnace at 950 °C for 1 h using a porcelain crucible. The melt was poured onto a pre heated brass mold and annealed at 360 °C for 8 h to remove thermal strains acquired by the glass matrix during sudden quenching. The glass samples were slowly cooled to room temperature, shaped and polished to

Table 1
Measured and calculated physical properties for 1.0 mol% Nd^{3+}-doped LCZSFB glass.

Physical quantities	LCZSFB
Sample thickness (cm)	0.300
Refractive index (n)	1.590
Density (g/cm^3)	4.880
Concentration (mol/l)	0.257
Concentration (ions $cm^{-3} \times 10^{20}$)	1.548
Average molecular weight (g)	190.230
Dielectric constant (ε)	2.528
Molar volume V_m (cm^3/mol)	38.980
Glass molar refractivity (cm^{-3})	13.150
Electronic polarizability α_e ($\times 10^{-24}$ cm^3)	5.220
Reflection losses R (%)	5.190
Polaron radius r_p (Å)	7.500
Inter ionic distance r_i (Å)	18.620
Field strength F ($\times 10^{14}$ cm^{-2})	5.300