Optical Materials 75 (2018) 357–366

Contents lists available at ScienceDirect

Optical Materials

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

Nd^{3+}-doped lanthanum lead boro-tellurite glass for lasing and amplification applications

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A R T I C L E I N F O

Article history:
Received 5 July 2017
Received in revised form
21 October 2017
Accepted 23 October 2017

Keywords:
Nd^{3+} ion: LBPT glasses
Judd-Ofelt
Luminescence quenching
Single exponential behaviour

A B S T R A C T

Nd^{3+}-doped lanthanum lead boro-tellurite glass samples were prepared by conventional melt quenching method and their structural, thermal, fluorescence, and decay times of the glasses were investigated. Prepared glass samples exhibits amorphous nature and shows good thermal stability in the temperature range of 100–800 °C. Judd-Ofelt (JO) analysis was carried out and the intensity parameters ($\Omega_{\lambda = 2, 4, 6}$) also spontaneous radiative probability and stimulated-.emission cross-sections were estimated. The magnitude of Ω_λ confirms the covalency nature. The near infrared emission spectra were measured by 808 nm excitation in which the emission intensity is found to be high at 1060 nm for the $^4F_{3/2} \rightarrow {}^4F_{11/2}$ transition. The stimulated cross section, effective band width and branching ratios are found to be 8.910×10^{-20} cm^2, 21.57 nm and 53.72 % respectively, for $^4F_{3/2} \rightarrow {}^4F_{11/2}$ transition. The derived gain bandwidth, figure of merit, threshold and saturation intensity found to be comparable to some of the glass systems. Furthermore, the time decay rate found to decrease from 100 μs to 27 μs when the concentration increased from 0.1 to 3.0 mol% of Nd^{3+} ions and also all follow the single exponential behaviour which is attributed to the self quenching effect due to the cross-relaxation channels.

1. Introduction

Rare earth (RE) ion doped glasses are the most promising candidates in the present technology and finds numerous applications in the field of fluorescent display devices, optical detectors, bulk lasers, optical fibres waveguide lasers [1–3] and fiber grating [4–6]. Now a day's rapid development is observed in the diode-pumped solid-state laser technology therefore research on more efficient new laser materials has gained much importance [1–3]. In this regard Nd^{3+} ion laser material is widely in use for different glasses and crystals upon exciting 808 and 885 nm laser diode excitation to develop high peak-power solid state lasers in the near infra-red (NIR) region at 1064 nm as it operates in 4 level mode with high gain cross sections [7–9]. The most probable lasing emission due to Nd^{3+} ion is in the wavelength region ~1060 nm, which is comprehensively useful. Along with these, Nd^{3+} ions can give lasing emission at 1800 nm, 1350 nm and 880 nm [10,11]. The efficient laser requires long fluorescence lifetime for $^4F_{3/2}$ level of Nd^{3+} ion which is influenced by non-radiative decay due to multiphonon relaxation and energy transfer process i.e. self quenching of emission due to Nd^{3+} ions pair interaction [12–15].

Some commercial glass system (LHG80, LG770, Q-88, LHG-8, LG750) have high stimulated emission cross section ranging from $3.6 - 4.2 \times 10^{-22}$ cm^2 [13,16,17] proves to be potential candidates for lasing applications. It is also reported that along with high stimulated emission cross section, high band width, low threshold, high gain and with suitable branching ratio will serve the practical demands. Choosing a suitable host material as laser active medium one can achieve the desired characteristics for a good performance such as high gain, high energy storage capability and minimum optical losses. In general, the Gain and energy storage capability depend on the stimulated emission cross-section, fluorescence lifetime and coupling efficiency of the pump source [13,16,17].

Among all the glass formers, borate glasses having high transparency, low melting point, high thermal stability and due to its good glass forming nature, they have been identified as more useful host matrices. Borate glasses containing heavy metal oxides can give intense fluorescence in the visible spectral region which is used as electro optic modulators, electro-optic switches,

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https://doi.org/10.1016/j.optmat.2017.10.037

solid state laser materials and non-linear parametric converters [18,19]. As the phonon energy of borate glass is 1400 cm^{-1} on addition of small amount of TeO_2 (700 cm^{-1}) [4] into the borate network improves the transparency and refractive index of the glass material as it is the key requirement for practical applications such as solid state lasers [20]. The other advantage of tellurite based glasses is that the Te–O bonds in such glass systems are weak and can be easily broken as a result rare earth ions and heavy metal oxides can be easily accommodated [21]. Therefore in the present work, Nd^{3+} ions doped lanthanum lead borotellurite glasses were prepared and extensively studied for their feasibility towards laser applications. In addition to the optical properties, theoretical model JO calculations are carried out to account for the line strength, intensity parameters, radiative and non-radiative properties and efficiency of the rare earth ion in the present glass matrix.

2. Materials and methods

2.1. Synthesis

The conventional melt quenching technique was adopted to synthesize $5La_2O_3$–$15PbO$-$(50-x)B_2O_3$-$(x)Nd_2O_3$–$30TeO_2$ (where x = 0, 0.1, 0.5, 1, 2 and 3 mol %) glasses, which will be labelled as LPBTN0, LPBTN01, LPBTN05, LPBTN1, LPBTN2 and LPBTN3 respectively. The starting materials of AR graded La_2O_3, PbO, H_3BO_3, TeO_2 and Nd_2O_3 procured from Sigma Aldrich were used directly without further purification. All the starting materials La_2O_3, PbO, H_3BO_3, TeO_2 and Nd_2O_3 are weighed according to the stoichiometric compositions such that to obtain about 10 gm per batch. All these materials are mixed thoroughly and grinded continuously for about 30 min using agate and motor. The obtained homogeneous mixture was then transferred in to the porcelain crucible, which is then kept in the muffle furnace. The mixture is melted at 1150 °C for 1hr to obtain complete and homogeneous melting (molten liquid). The obtained homogeneous molten liquid was quickly poured on to a brass moulds and quenched quickly to avoid the crystallization of glass materials. Prior to quenching, the brass moulds were preheated. Quenched samples were further annealed at 350 °C for 8 hr in muffle furnace and cooled slowly till room temperature is attainted to remove thermal induced stress and strain associated with the prepared samples during quenching.

2.2. Characterization

Prepared glass samples were characterized through x-ray diffractometer (XRD), RIGAKU, ULTIMA IV, 40 kV, 30 mA, using Cu K_α radiation of wavelength λ = 1.5406 Å. Optical parameter, Refractive index is measured using digital Abbe refractometer ATAGO of wavelength 589.3 nm of accuracy up to ±0.0002. The density of the prepared glass samples was determined from Archimedes principle using toluene (ρ = 0.866 gm/cm^3) as an immersion liquid. Fourier Transform Infra-Red spectroscope (FTIR) measurements were carried out with resolution of 4 cm^{-1} in the spectral range 400 cm^{-1} to 4000 cm^{-1} using Thermo Nicolet, Avatar 370 following KBR pellet technique. For thermal studies, DTA/TGA analysis were carried out with nitrogen atmosphere using Perkin Elmer model, in the temperature range RT to 800 °C at a heating rate of 10 °C/min. Optical absorption spectra were recorded by Perkin Elmer 300 nm–1100 nm. Luminescence studies and time decay measurements were done using EDINBURGH FLS, 808 nm laser diode for IR range which as sensitivity >25,000:1 standard.

3. Results and discussion

3.1. Physical properties

The physical parameters for LPBTN1 glass were determined and are summarized in Table 1. Also, several physical properties such as neodymium ion concentration (N_i), inter ionic distance (r_i), polaron radius (r_p) and field **s**trength (F) were determined using the equations given in literature [22,23] for LBPTN1 glass sample. The density and average molecular weight values further used to evaluate the concentration of luminescent (Nd) ions in the glass matrix. It is found that the concentration of luminescent (Nd) centers (N_i) are densely distributed in the glass matrix which is evidenced from the higher values of the glass density (d) and refractive index (n). The estimated polaron radius (r_p) is found to be 2.5 times smaller in size compared with the inter-ionic distance (r_i), which results in the higher field strength 0.92 × 10^{15} cm^2.

3.2. X-ray diffraction (XRD)

XRD patterns of prepared Nd doped LPBT glass samples are depicted in Fig. 1. It is seen that, patterns exhibits no crystalline peaks except broad hump in the region 20° – 40°, which confirms the amorphous nature of the glass samples [7,9,21]. It is also observed that, even after addition of Nd^{3+} into the glass network, it has not induced crystalline in the material. Hence all the prepared samples are in amorphous state showing glassy nature.

3.3. Fourier Transform Infra-Red (FTIR) studies

FTIR spectra in the range of 400 – 4000 cm^{-1} for Nd doped LPBT glass samples are depicted in Fig. 2. It is seen that, the FTIR spectra exhibit several stretching/bending vibrational bands, which gives information about the local structure of the prepared glass samples. It is observed that, all the samples exhibit distinct features/bands at or around 685, 930, 1070, 1250, 1360 and 2350 cm^{-1}. These observed bands are assigned based on the available literature on LPBT glasses [24–30]. The bands observed at around 685 cm^{-1} is assigned to anti-symmetric vibrations of Te–O–Te linkages constructed by two un-equivalent Te–O bonds in trigonal pyramid of TeO_3 units associated with the non-bridging oxygen, which is the characteristic peak of TeO_2 based glasses [25–27]. The bands observed in IR the region of 800–1200 cm^{-1} and 1200–1400 cm^{-1} corresponds to the B–O bond stretching in BO_4 groups and the vibration of the B–O bond in BO_3 groups [24–26] respectively. In particular, the observed bands at or around 930 cm^{-1} and 1070 cm^{-1} are mainly due to the B–O–B bending vibrations in BO_4 units. Whereas, the bands at 1250 cm^{-1} and 1360 cm^{-1} are

Table 1
Summary of estimated physical parameters of LPBTN1 glass sample.

Physical parameters	Values
Molecular weight (M.W)g	135.79
Refractive index (n)	1.652
Thickness (t) mm	3.28
Concentration (N_i) × 10^{20} ions/cc	3.68
Density (ρ)g/cm^3	4.125
Molar volume (V_m)g/cm^3	41.20
Molar refractivity ($R_{m)}$ cm^{-3}	15.06
Molar polarizability (α_m) × $10^{-24}cm^3$	5.96
Polaron radius (r_p)nm	0.57
Inter ionic distance (r_i)nm	1.41
Field strength (F) × $10^{15}cm^2$	0.92
Dielectric constant (ε)	2.729
Reflection loss (R_L)%	6.04