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RESEARCH ARTICLE

Neodymium Doped Borate Glasses for NIR Emitting Solid State Device Applications

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Abstract

Objectives: To investigate the effect of B_2O_3 replaced by Nd_2O_3 studies on the spectroscopic characteristics of trivalent neodymium (Nd^{3+})-doped glasses using XRD, FTIR, absorption, and emission spectroscopy. **Methods:** The glasses were synthesized using the conventional melt quenching technique at 1150^0 C. The amorphous nature of the samples was confirmed by x-ray diffraction studies. **Findings:** The addition of Nd_2O_3 concentration affects the absorption and emission properties of the Nd^{3+} ion measured in the near-infrared luminescence range from 0.9μm, 1.06 μm, and 1.36μm associated with the $^4F_{3/2}\rightarrow{}^4I_J$ (J = 9/2, 11/2, 13/2) transitions. **Novelty:** The novelty of the present work is to fully understand and characterize the luminescence of Nd^{3+} doped borate bulk glasses with different doping concentrations. So as to gain an insight of 1.06 μm corresponding to $^4F_{3/2}\rightarrow{}^4F_{11/2}$ transition, these glasses are highly potential one which is an applicable to NIR emitting solid state device.

Keywords: Nd3+ ions; FTIR; UV; Photoluminescence; Borate glasses

1 Introduction

Glasses are the most advanced material in terms of technology and are utilized in a wide range of applications. They are notable for being optically transparent and brittle. Due to their wide range of prospective uses and applications in the design and development of photonic devices, the rare-earth (RE) doped glass materials have attracted a lot of attention(1,2).

Due to their high transparency, low melting point, great thermal stability, and potent solubilities in rare earth ions, borate-based glass hosts have been demonstrated to be capable of lasing in the NIR range. A particularly good optical medium are borate glasses(3). The addition of alkaline element improves the chemical stability by modifying the glass network due to their charge transfer with the neighbor host element(4).

Optical material activated by Nd^{3+} ions are very interesting for emitting devices. Especially Nd^{3+} ions are very attractive active media for powerful solid-state laser working in the NIR spectral region(5). Dinesh Kumar et.al (2019) had studied Nd^{3+} doped sodium strontium borate glasses their results shows that their prepared glasses are suitable for thermoluminescence device materials(6).

Photoluminescence properties have not been investigated.

Kashif. et. al (2020) had studied Nd^{3+} ion dopedlithium borate glasses their result shows their prepared glasses are the potential for application of “photovoltaics” (7). they have not studied NIR emitting solid state device applications Y. S. Ramah et. al (2022) had studied cadmium lead-borate glasses doped with Nd^{3+} ions and their investigations show that the materials are applicable for optoelectronics and photo electric devices (8). NIR emitting device applications have not been studied.

In our work we focus on the optical properties of Nd^{3+} ions doped in Calcium -Aluminum-Borate-Barium-Sodium glass matrix. The direct and indirect band gaps Nd^{3+} concentration dependent was evaluated. The optical properties of $CaO-Al_2O_3-BaO-B_2O_3-Na-Nd_2O_3$ (where x=0.1,0.3, and 0.5 mol%) host glass were optimized for Nd^{3+} concentration and understand the feasibility of using it for NIR emitting solid state device applications.

2 Methodology

The glass system of $23CaO-10Al_2O_3-(51-X)\ B_2O_3-6BaO-10Na_2O-XNd_2O_3$ where X=0.1,0.3, and 0.5, (coded as CaAlBBaNaNd0.1, CaAlBBaNaNd0.3, CaAlBBaNaNd0.5 mol%) where prepared by conventional melt quenching technique. The high purity chemicals $CaCO_3$, Al_2O_3, H_3BO_3, $BaCO_3$, Na_2CO_3, and Nd_2O_3 were mixed and grinded by using agate, mortar to make fine powder and the total amount of each batch of glass formula was thoroughly mixed till it obtained a homogeneous mixture and weighed to 15 gm. a porcelain crucible with well grinded oxides was used to place the uniform mixture in electrical muffle furnace. Density (ρ) measurements on glass samples were performed using the Archimedes technique using toluene as the immersion solvent. The prepared mixture was then heated at 1150^0 C for 3hours, the homogeneous oxides melt remained and then swiftly dispensed into stainless steel block that had been pre - heated, and it was quenched to create uniform thick glass samples. To reduce thermal stress, the glass underwent an entire day of annealing at 550^0C before being allowed to cool gradually to ambient temperature. The powdered approach was utilized to capture the X-ray diffraction pattern of glass samples. CuKα with a wavelength of 1.54 nm, was employed as a source in the Diffractometer. The FTIR spectra were recorded at room temperature using Perkin Elmer Lambda PRONTIER (MIV-FTIR) The acquired glass sample were shaped for characterization. Using Perkin Elmer lambda 950 UV/VIS/NIR spectrophotometer, the optical absorption spectra of present glass were measured in UV/VIS/NIR region of 250-2500nm. The photoluminescence spectra were recorded using near-infrared spectrophotometers (Quanta Master (QM)-300, PTI-Horiba) using Xenon as a source.

3 Result and Discussion

3.1 Physical properties

Table 1. Glass samples with different compositions

Samples	**Glass composition (mol%)**
(N1) $CaAlBBaNaNd_{0.1}$	$23CaO-10Al_2O_3-50.9B_2O_{3-}6BaO-10Na_2O–0.1Nd_2O_3$
(N2) $CaAlBBaNaNd_{0.3}$	$23CaO-10Al_2O_3-50.7B_2O_{3-}6BaO-10Na_2O–0.3Nd_2O_3$
(N3) $CaAlBBaNaNd_{0.5}$	$23CaO-10Al_2O_3-50.5B_2O_{3-}6BaO-10Na_2O–0.5Nd_2O_3$

Table 2. Physical properties of Nd_2O_3 concentration doped in oxide borate glasses

Physical properties	**N1**	**N2**	**N3**
Density(g/cm^3)	2.55	1.92	2.57
Molar volume(cm^3/mol)	29.54	38.96	29.34
Refractive index (n)	1.57	1.57	1.57
Dielectric constant(⊠)	2.46	2.46	2.46
Nd^{3+}ionconcentration ($x10^{21} ions/cm^3$)	20.45	15.39	20.63
Polaron radius (A°)	5.57	4.25	3.26
Interionic distance r_i(A°)	7.61	5.81	4.46
Field Strength ($Fx10^{20}$)cm^{-2}	9.64	1.65	2.80
Average boron-boron separation (d_{B-B})(A°)	2.25	2.48	2.25
Molar refraction (R)(cm^3/mol)	9.55	12.78	9.62
Molar cation polarizability (α_{cat})	3.79	5.07	3.82
No. of oxides in chemical formula ($N_{O2}{}^-$)	2.22	2.22	2.22

Continued on next page

Table 2 continued

Electronic oxide polarizability (α_{o2-}n)	1.60	2.17	1.61
Optical basicity(Λ)	0.62	0.90	0.63
Metallization Criteria(M)	0.86	0.86	0.86
Theoretical Basicity(Λ_{theo})	0.69	0.69	0.69

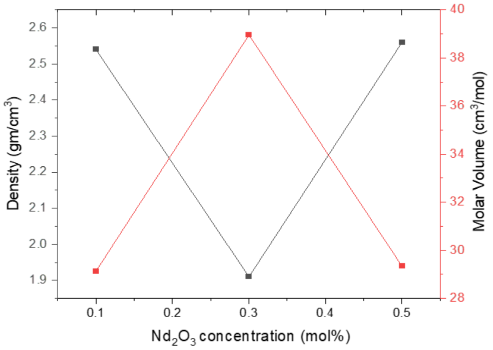

Fig 1. Density, Molar volume Vs concentration of Nd_2O_3

3.1.1 Density, molar volume and dielectric constant

With the addition of Nd_2O_3, the samples' average molecular weight rises. Since (Nd_2O_3), which has a greater molecular weight (336.4782), substitutes (B_2O_3), which has a lower molecular weight (69.6202), this is evident. In relation to the geometrical configuration, cross-link density, interstitial space sizes, coordination number, and refractive index, changes in the density of the glass can have an impact on the optical band gaps of the glass system. The density values in the current glass are 2.55, 1.92, and 2.57; following the first value, the second value decreased to 1.92; the first value increases as a result of the substitution of Nd_2O_3 with B_2O_3, which has a greater molecular weight. While the creation of non-bridging oxygen (NBO) atoms in the glass matrix may be responsible for the drop-in density in the second sample. The nature of the glass density and the modifying impact of neodymium ions by producing interstitial gaps with NBO in the glass matrix are credited with the trend of the molar volume of its values. Due to the excessive dopant concentration in the glass, the polaron radius and interionic distance shrank as the concentration of neodymium ions rose. The other physical parameters like field strength, average boron-boron separation, molar cation polarizability, electronic optical polarizability, optical basicity, metallization criteria were calculated using the relations given in literatures(9,10).

3.2 X-Ray Diffraction Studies

The Figure 2 shows the X-ray diffraction profiles of all the glass samples doped with Nd^{3+} ions. For all of the samples, the diffracted intensity was measured for the angular distribution of scattered x-ray energy between 0^0 and 100^0. No sharp peaks were observed in XRD spectra indicating that all of the synthesized CaAlBBaNaNd glass samples are amorphous in nature(11).

3.3 IR Studies

The analysis of IR spectra can reveal information on the rotation and vibration of different molecules within a glass matrix. The features of a molecule's vibrations are related to frequency; these vibrations are distinct from those of other groups of molecules in the matrix and each has a unique characteristic of vibrational frequency. The above figure show the CaAlBBaNaNd glasses' recorded Fourier transform infrared spectra at room temperature. The spectrum shows eight conventional bands coming from different elements in the current glasses doped with Nd^{3+} ions and it reflects the functional groups of the glass matrix. The significant changes in the band positions are observed from Figure 3. In the prepared glass samples the peaks were located at 411cm^{-1},544cm^{-1},672cm^{-1} ,826cm^{-1}, 1227cm^{-1},1659cm-^{1}, 2974cm^{-1}, 3389cm^{-1}.

The intensities of these bands differ from one composition to another. The band observed at 400-500cm is due to Ca^{2+} cation vibrations. The second band observed at 769-1200 cm^{-1} due to presence of B-O bond stretching in BO^{4-} structural unit from a diborate group. The band observed at 1200-1569 due to the stretching vibrations of NBOs

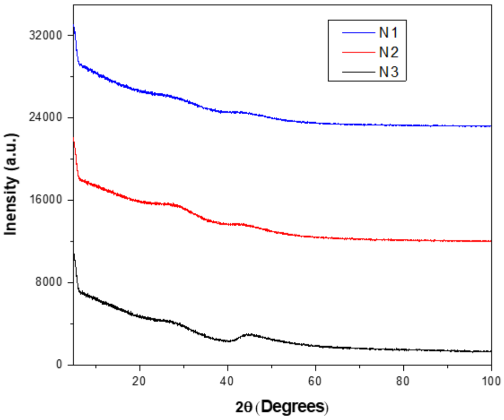

Fig 2. X-Ray diffraction patterns of CaAlBBaNaNd glasses

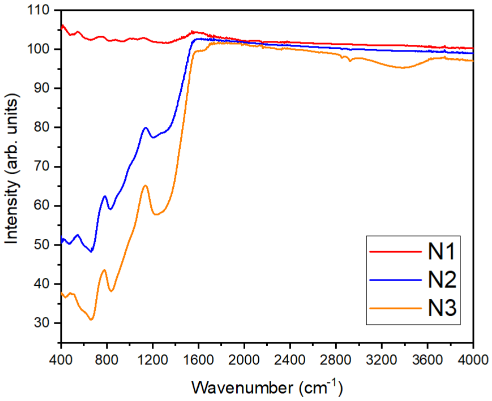

Fig 3. FTIR of CaAlBBaNaNd glasses

of trigonal units of BO_3. The existence of symmetric hydrogen bond (OH) group vibrations in the referred glasses is what causes the final strong broad band at 3389 cm^{-1}. Alkali and alkali earth elements, which have functional fundamental properties vibrational wave number for the pertinent element groups present in the glass network, are present in the glass network during the formation of the glass network, which results in the bands seen in the spectrum(12).

3.4 Optical Absorption studies

The absorbance studies of 23CaO–10Al_2O_3–(51-x)B_2O_3-6BaO-xNd_2O_3_10Na_2O- glass doped with various concentrations of Nd_2O_3 are calculated in UV–VIS-NIR recorded at room temperature in the wavelength range of 300-1000nm is shown in Figure 4 . The optical absorption spectra of the studied glass the optical absorption of spectra consists of ten transitions that are originated from $^4I_{9/2}$, level various excited level including $^4D7_{/2,}$ $^2D_{5/2,}$ $^{2G}9_{/2,}$ $^4G_{7/2,}$ $^4G_{7/2} + {}^4G_{5/2,}$ $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2,}$ $^4F_{5/2}$ and $^4F_{3/2}$ States which are peaked at 348,427, 470, 509, 523, 580, 622, 678, 745, 802, and 866nm respectively. The spectral shapes and positions of these transitions are similar to reported ones. As can be seen from Figure 4 the strongest transitions called hyper-sensitive transitions centered at 580 nm due to transition from $^4I_{9/2}$ level $^2G_{7/2} + {}^4G_{5/2,}$ level the hyper sensitive fallows the quadrupole selection rules $\Delta J \leq 2$; $\Delta L \leq 2$; $\Delta S \leq O$.

The optical band gap energy as illustrated in Figure 5 (direct band gap) and Figure 6 (indirect band gap) extrapolates the absorption edge of the graph. As indicated in the table, the addition of Nd_2O_3 concentration causes both the direct and indirect band gap energy of the glasses to grow. The direct and indirect band gap energy of the glasses is determined to be in the range of 3.54 to 3.65 eV and 3.24 to 3.41 eV, respectively. The optical band gap of the glass system is impacted by such structural modifications brought about by the insertion of Nd^{3+} ions. When Nd^{3+} ions are added to glasses, the glass's structure changes,

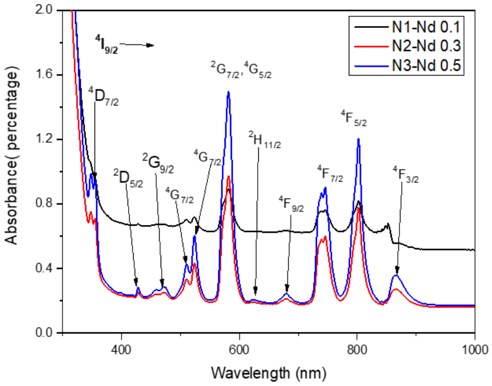

Fig 4. UV–Vis–NIR absorbance of CaAlBBaNaNd glasses

and this has an impact on the optical band gap's values [13,14].

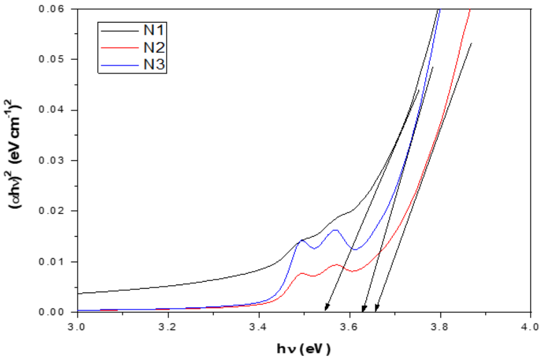

Fig 5. Direct Optical Band Gap of CaAlBBaNaNd glasses

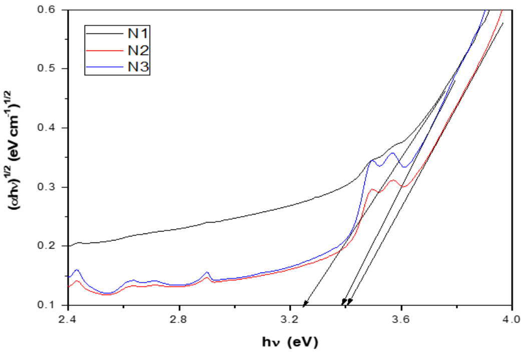

Fig 6. Indirect Optical Band Gap of CaAlBBaNaNd glasses

Table 3. Direct /Indirect optical band gap of the prepared Nd^{3+} glasses

Sl.No.	Glasses	Direct band gap (eV)	Indirect band gap (eV)	
01	(N1) CaAlBBaNaNd0.1	3.54	3.24	Present work
02	(N2) CaAlBBaNaNd0.3	3.65	3.41	Present work
03	(N3) CaAlBBaNaNd0.5	3.62	3.38	Present work
04	M1 (borate :ca+al+na)	3.835	3.363	(15)
05	Nd 0.5	3.51	3.14	(16)
06	BBaAzNd	3.40	3.15	(17)

3.5 Luminescence studies

3.5.1 NIR-Emission spectra

The NIR emission spectra of Nd3^{+} ions doped CaAlBBaNaNd glasses under 582 nm excitation wavelength were recorded and shown in the Figure 7 It was focused 3 emission bands at 903, 1074, and 1345nm, these peaks were assigned as $^{4}F_{3/2\rightarrow}$to $^{4}I_{9/2,}$ $^{4}F_{3/2}$ to and $^{4}F_{3/2}$ to $^{4}I_{13/2}$ respectively $^{4}I_{11/2}$theemission spectra here assigned by comparing the band positions in the emission spectra with these reported in the literature. Among them the emission band at 1074nm corresponding to $^{4}F_{3/2}$to $^{4}I_{11/2}$transitions is the most intense and sharp. It can be seen from the emission spectra that by varying the doping concentration in the glass system, the emission intensity increases up to 0.3 mol% of neodymium before decreasing. It can be observed that during increasing concentration from 0.1 mol% to 0.5mol% of Neodymium, emission intensity is enhanced two-fold times and then decreases. The concentration quenching effect can also be seen when added in higher concentration of Nd_2O_3 content(18,19). The intensity of the emission increases with increasing Nd_2O_3 content, and the transition $^{4}F_{3/2}$ to $^{4}I_{11/2}$ corresponding to 1074 nm whereas the reported literature shows at 1049 nm(20) and 1066 nm(21).

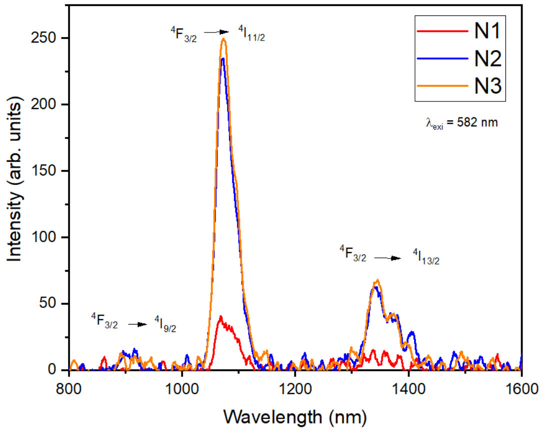

Fig 7. Photo luminescence Spectra ofCaAlBBaNaNd glasses monitored at 582nm

4 Conclusion

The glasses were prepared using melt quenching technique. With the addition of Nd_2O_3, the samples' show average molecular weight increases. The absorbance studies of 23CaO–10Al_2O_3–(51-x) B_2O_3-6BaO-10Na_2O glass doped with various concentrations of Nd_2O_3 are evaluated using UV–VIS-NIR. Amorphous nature of the glass was confirmed by X-ray diffraction study. Signature bands of borate network was observed especially BO_3 and BO_4 vibrational units were observed using Fourier transform infra-red spectra. Excitation of 582 nm was used as source to excite the Nd^{3+} ions in CaAlBBaNaNd glass from $^{4}I_{9/2}$ ground state to $^{4}F_{3/2}$ excited state the peaks corresponding to $^{4}F_{3/2}$ to $^{4}I_{9/2}$ and $^{4}F_{3/2}$ to $^{4}F_{13/2}$ are absorbed at 1074 and 1341nm respectively among two bands a transitions corresponds to $^{4}F_{3/2}\rightarrow{}^{4}I_{11/2}$ (1074nm) is a potential laser transition having high intensity than the remaining transitions for all the as prepared glasses. These glasses are potential candidates for NIR emitting solid state device applications.

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