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NIR emission of Nd^{3+}-doped sodium barium borate oxyfluoride glasses for 1.07 μm laser materials

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Abstract

Glass samples with varying concentrations of Nd_2O_3 were prepared by using the melt-quenching technique. The absorption spectra and the NIR emission spectra of Nd^{3+}-doped sodium barium borate oxyfluoride glasses were investigated in order to understand the effect of different Nd_2O_3 concentrations. The absorption spectra exhibited eight peaks in the visible light range and three peaks in NIR range. All of transition peaks were found to start from a transition ground state of $^4I_{9/2}$ and move to excited states. The transition of $^4G_{5/2}+^2G_{7/2}$ gave the largest peak when compared to the other transition peaks that were observed. The absorbance of the glass samples was seen to increase as a function of Nd2O3 concentration. The emission spectra were found at wavelengths of 1071 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1343 ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) nm. The transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ shows that the material has great potential for use as a laser material as it has a wavelength of 1071 nm. The emission intensity was seen to increase with Nd_2O_3 concentration up to 0.50 mol%. Increasing the concentration beyond this point led to a fall in emission intensity. It was thought that this was due to the concentration quenching effect.

Keywords: Optical absorption, Nd2O3, NIR emission, sodium barium borate glasses
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1. Introduction

Various research has been carried out in order to develop suitable host materials for useful photonic applications [1]. Among these materials, glass is the one which attracts the most attention. This is due to its low cost, simple manufacturing process, strength and high ability to contain embedded ions [2-4]. Embedding trivalent rare earth (RE^{3+}) ions into glass can enhance its optical and luminescence properties. This is because 4f-4f and 4f-5d electronic transitions are shielded by 5s and 5p outer shells [5-7]. The improvement in properties of glass from the addition of RE^{3+} ions rely on two factors. These are the class of the host glass and the concentration of RE^{3+} ions within it [8]. Of the possible host glasses, borate oxide glasses are one of the most appropriate for doping with RE^{3+} ions. This is on account of its low melting point, high transparency, high thermal stability and excellent properties as a solvent from RE^{3+} ions [9-10]. The improvements in luminescence properties however, need to consider the non-radiative process by multiphonon relaxation. This should be as low as possible [11]. Borate glass has a phonon energy of approximately1,400 cm-1 [12]. This is higher than phosphate (1,200 cm^{-1}), silicate (1,100 cm^{-1}) and tellurite (600-800 cm^{-1}) oxide glasses [13-14]. This drawback can be overcome by adding BaO to the glass. BaO also has the impact of reducing the transition probability of non-radiative decays which in turn improves the glass' luminescence properties [15-16]. The luminescence efficiency of borate oxide glasses is lower than borate fluoride glasses thanks to lower vibration energies. Glass produced with borate fluoride glasses has poor mechanical properties and poor chemical durability. These limit the usefully applications of the glass. Borate oxyfluoride glasses have the advantages of both the oxide and fluoride chemical compositions. These benefits include good mechanical stability, good chemical stability and high luminescence efficiency.

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They were therefore chosen for use as host glass for this research. [17-18]. In this research NaF was added to the glass instead of NaO as the F^- ions in NaF decrease the hydroxyl (OH) group in the host glass by reacting with OH to hydroxyl fluoride (HF) [19]. This was clearly advantageous as it increases the luminescence efficiency. NaF also has the impact of reducing the melting temperature of the glass as well as reducing defects and bubbles in its structure [20-21].

When experimenting with glass containing RE^{3+} ions, Nd^{3+} ions are the most of suitable for Near-Infrared (NIR) laser materials. This is due to the glass' emissions which occur at approximately 900 nm ($^4F_{3/2}\rightarrow{}^4I_{9/2}$), 1060nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1330 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$) under the correct excitation wavelength [8]. The transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is particularly important for 1060 laser materials as it gives the strongest peak in all of the emission peaks of Nd^{3+} ions [17]. A large amount of research is available giving details of investigations into Nd^{3+}-doped glasses. Lalla *et al.* presented the optical absorption and luminescence properties of Nd^{3+}-doped TeO_2-PbF_2-AlF_3 glasses for laser applications [2], Yu *et al.* studied spectroscopic properties of Nd-doped Bi_2O_3-GeO_2/SiO_2 glasses [5], Binnemans *et al.* studied optical properties of Nd^{3+}-doped fluorophosphates glasses [22], Nie *et al.* investigated the 1.3 μm emission of Nd^{3+}-doped bismuth-based oxide glasses [23], Raju *et al.* presented the Judd-Ofelt analysis and photoluminescence properties of Nd^{3+} in cadmium lithium boro tellurite glasses [24]. According to the research, adding Nd_2O_3 to glass can enhance its optical and luminescence properties of glasses. Increasing Nd_2O_3 content in glass, however, does have restrictions. This is due to concentration quenching effect when the concentration reaches a certain level [25] This research, therefore, aimed to identify the highest emission levels of various Nd_2O_3 concentrations in sodium barium borate oxyfluoride glasses suitable for becoming 1.07 μm laser materials [26]. The physical, optical and NIR luminescence properties have been investigated for glass samples produced with various Nd_2O_3 concentrations.

2. Materials and Methods

2.1. Preparation of glass samples

The chemical composition of the glass samples that were produced can be seen in Table 1. The glass was prepared using the melt quenching technique. Analytical reagent grade chemicals were used for this research. They were sodium fluoride (NaF), barium carbonate (Ba_2CO_3), boric acid (H_3BO_3) and neodymium oxide (Nd_2O_3). The chemicals were mixed in an alumina crucible and then were melted at temperature 1,200 °C for 3 hours. Afterwards the melts were poured on a graphite plate and were annealed at a temperature of 500 °C for 3 hours before being cooled down to room temperature. Finally all of the glass samples were cut to the dimensions 1.0cm × 2.0cm × 0.3 cm and were polished to prepare them for analysis.

2.2. Measurements

The densities (ρ) of the samples were measured using the Archimedes principle using water as the immersion liquid. The molar volumes (V_m) were calculated using the equation that follows:

$$V_m = \frac{M_T}{\rho} \quad (1)$$

In which V_m is molar volume (cm^3/mol), M_T is the molecular weight of the glass sample (g/mol) and ρ is the density (g/cm^3) of the sample. The refractive indexes of the samples were measured using an Abbe refractometer with wavelength 589.3 nm. A sodium-vapour lamp was used as the light source and 1-bromonaphthalene ($C_{10}H_7Br$) was used as an adhesive coating for shielding the gap between prism of refractometer and the sample. The optical absorption spectrum of the samples was measured using a UV-VIS-NIR spectrophotometer (Shimazu, UV3600). A xenon light source was used with wavelengths ranging from 400 to 950 nm. The NIR emission spectrum of the samples was measured using a fluorescence spectrometer (Quanta Master 300, Photon Technology International). Again a xenon flash lamp was used as the light source. A photomultiplier tube (InGaAs detector) was used to detect NIR emission.

3. Results and Discussion

The molecular weights, densities, molar volumes and refractive indexes of the samples are shown in Table 2. It was found that the densities of the samples increased with increasing Nd_2O_3 concentration. This was because the substitution of B_2O_3 (Mw = 69.6202 g/mol) by Nd_2O_3 (Mw = 336.4822 g/mol) resulted in increasing the sample's overall molecular weight [17]. This variation of density is shown in Figure 1. The molar volumes of the samples were also found to increase with Nd_2O_3 concentration as shown in Figure 2. This indicated that the Nd^{3+} ions in in the glass broke bonds between boron and oxygen in its network. Figure 3 shows the variation of refractive index as a function of Nd_2O_3 concentration in the glass samples. Adding Nd_2O_3 to the samples had the effect of increasing its refractive indexes. This is due to the fact that the addition of Nd^{3+} ions can slow the speed of light in the glass. When speed of light in glass is slowed, the refractive index increases. This is because the refractive index of light (n) has a relationship with of the speed of light in a vacuum (c) and the speed of light in glass (v) as shown in the following equation [6].

$$n = \frac{c}{v} \quad (2)$$

Table 1. Chemical composition of Nd^{3+}-doped NBB oxyfluoride glasses.

Chemical composition **30NaF : 15BaO : (60-x)B_2O_3 : xNd_2O_3**	**Glass ID**
30NaF : 15BaO : 54.95B_2O_3 : 0.05Nd_2O_3	NBBNd005
30NaF : 15BaO : 54.95B_2O_3 : 0.10Nd_2O_3	NBBNd010
30NaF : 15BaO : 54.95B_2O_3 : 0.50Nd2$_2O_3$	NBBNd050
30NaF : 15BaO : 54.95B_2O_3 : 1.00Nd_2O_3	NBBNd100
30NaF : 15BaO : 54.95B_2O_3 : 2.00Nd_2O_3	NBBNd200
30NaF : 15BaO : 54.95B_2O_3 : 4.00Nd_2O_3	NBBNd400

Table 2. The densities, molar volumes and refractive indexes of the glass samples are shown in the following table.

Glass ID	**Molecular weight (g/mol)**	**Density (g/cm^3)**	**Molar volume (cm^3/mol)**	**Refractive index**
NBBNd005	74.0200	2.6623±0.0002	27.8028±0.0020	1.5296±0.0002
NBBNd010	74.1534	2.6652±0.0002	27.8225±0.0016	1.5306±0.0004
NBBNd050	75.2208	2.6795±0.0001	28.0724±0.0011	1.5319±0.0003
NBBNd100	76.5552	2.7148±0.0005	21.1994±0.0053	1.5340±0.0004
NBBNd200	79.2238	2.7674±0.0002	28.6273±0.0024	1.5380±0.0004
NBBNd400	84.5610	2.2879±0.0001	29.3623±0.0013	1.5461±0.0002

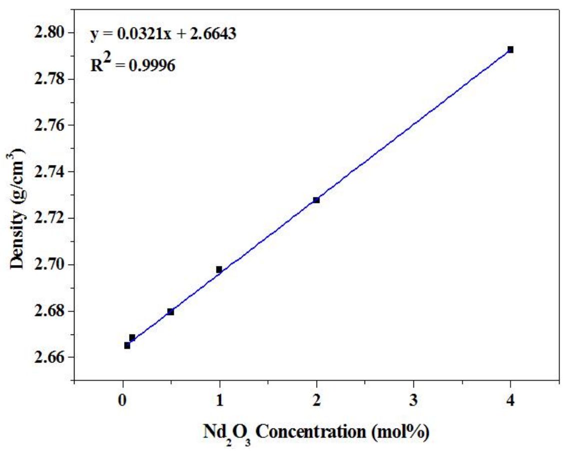

Figure 1: The variation of densities as a function of Nd_2O_3 contents in NBB oxyfluoride glasses.

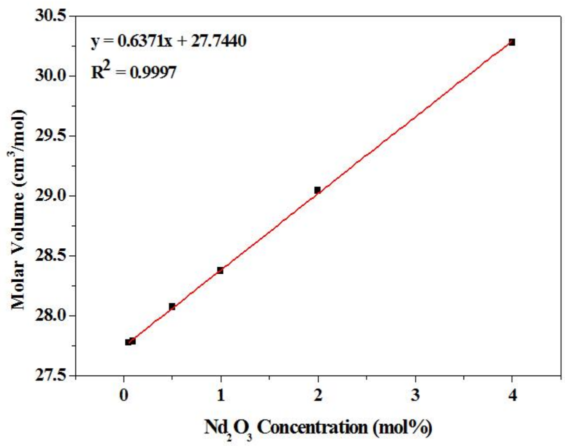

Figure 2: The variation of molar volumes as a function of Nd_2O_3 contents in NBB oxyfluoride glasses.

Where n is refractive index of glasses, c is speed of light in vacuum (3×10^8 m/s^2) and v is speed of light in the glass (m/s).

The optical absorption spectra of the samples was measured for the light wavelength range of 400-950 nm. These are shown in Figure 4. The specra were all found to comprise of eleven peaks due to the presence of Nd^{3+} ions. They were located at 429nm, 459nm, 474nm, 514nm, 526nm, 583nm, 628nm, 688nm, 747nm, 806nm and 874 nm. It was thought that these were caused by the movement from state $^4I_{9/2}$ to transition states $^2P_{1/2}+^2D_{5/2}$, $^2G_{9/2}+^2(D+P)_{3/2}$, $^2D_{3/2}+^2G_{9/2}+^4K_{15/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}+^2G_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4S_{3/2}+^4F_{7/2}$, $^4F_{5/2}+^2H_{9/2}$ and $^4F_{3/2}$, respectively [19, 20, 27]. Among all the absorption peaks, the transition $^4G_{5/2}+^2G_{7/2}$ gave rise to the strongest response. This is well known to be a hypersensitive transition according to the selection rules $|\Delta j| \leq 2, |\Delta L| \leq 2$ and $|\Delta S| = 0$. It's strength depends on the environment around the Nd^{3+} ions [11]. It is observed that the $^4G_{5/2}+^2G_{7/2}$ transition did not increased with increasing Nd_2O_3 concentrations.

The emission spectra of the Nd^{3+}-doped glass samples were measured in the NIR range from 800nm to 1400nm under the excitation at 583 nm as shown in Figure 5. The strongest peaks were observed at 1071nm and 1343 nm. These peaks corresponded to the transitions $^4F_{3/2} \rightarrow {^4I_{11/2}}$ and $^4F_{3/2} \rightarrow {^4I_{13/2}}$ respectively [26]. The transition $^4F_{3/2} \rightarrow {^4I_{11/2}}$ showed the highest emission intensity compared to the $^4F_{3/2} \rightarrow {^4I_{13/2}}$ transition. In fact it was around 3.6 times stonger at an Nd_2O_3 concentration of 0.05 mol%. This result

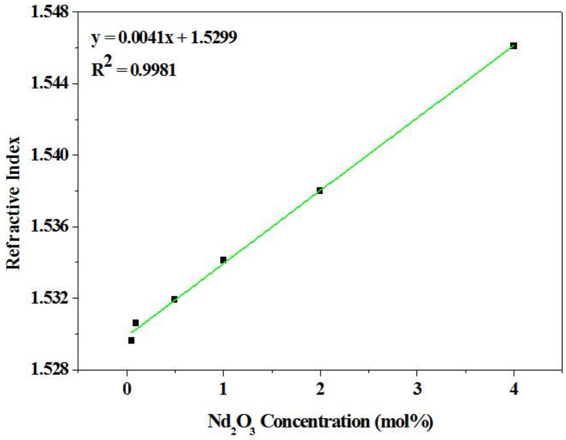

Figure 3: The variation of refractive indexes as a function of Nd_2O_3 concentration in NBB oxyfluoride glasses.

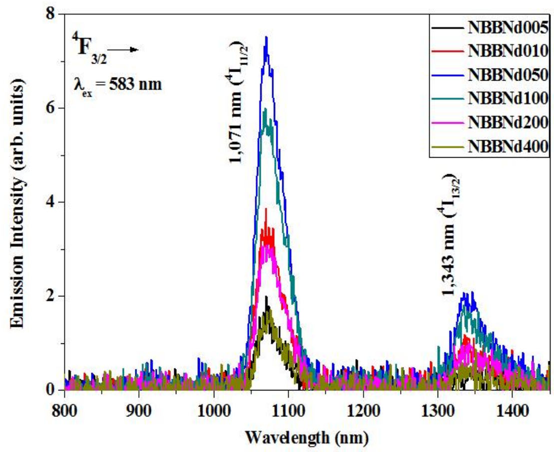

Figure 5: Emission spectra of Nd^{3+}-doped NBB oxyfluoride glass.

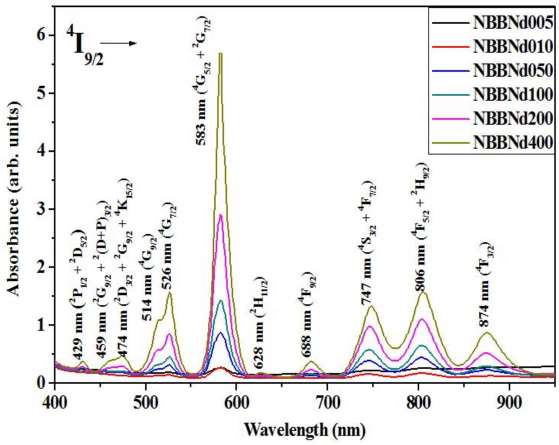

Figure 4: Optical absorption spectra of Nd^{3+}-doped NBB oxyfluoride glasses.

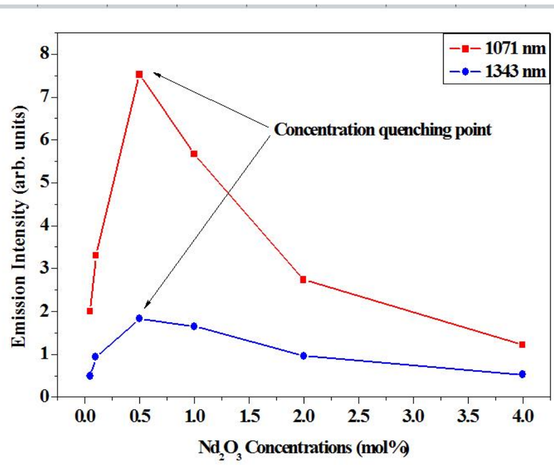

Figure 6: The variation of emission intensity as a function of Nd_2O_3 contents in NBB oxyfluoride glasses.

is shown in Figure 6. The transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ is was most relevant for materials which are used as 1.07 μm laser materials. It was found, however, that emission intensity increased along with Nd_2O_3 concentration up to 0.50 mol% and droped down beyond this. This reduction is known as the quenching effect. This is a result of the energy transfer through cross relaxation between Nd^{3+} and Nd^{3+} ions ($^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{15/2}$) [28] as shown in the partial level diagram shown in Figure 7. This diagram shows the exciation of Nd^{3+} ions from ground state, $^4I_{9/2}$ level, to excited state, $^4G_{5/2}$ + $^2G_{7/2}$ level. Following this there was a quick non-radiative relaxation (NRR) to $^4F_{3/2}$ level. After this the Nd^{3+} ions have only radiative relaxation to its lower energy levels. In contrast, the Nd^{3+} ions from ground state $^4I_{9/2}$ level excited to $^4I_{15/2}$ level at the same time and exchange energy between each other. This phenomenon is called cross relaxation and it has the result of reducing the overall emission intensity of Nd^{3+} ions [29]. From all of the samples that were made the 0.50 mol% of Nd_2O_3 samples was found to be the most suitable for use as a 1.07 μm laser material.

4. Conclusions

Oxyfluoride glass samples with differing concentrations of Nd^{3+} ions were prepared by melt-quenching technique. The samples were melted at a temperature 1,200 °C for 3 hours and then were annealed at temperature 500 °C f before being cooled down to room temperature. The physical, optical and NIR-luminescence properties of the glass samples were then characterized. It was found that the densities and refractive indexes of the glass samples tended to increase with Nd_2O_3 concentration. This was due to the fact that the molecular weight of Nd_2O_3 is higher than B_2O_3. The molar volume of the samples was also found to also increase with increasing Nd_2O_3 concentrations. This indicated the modifier behavior of

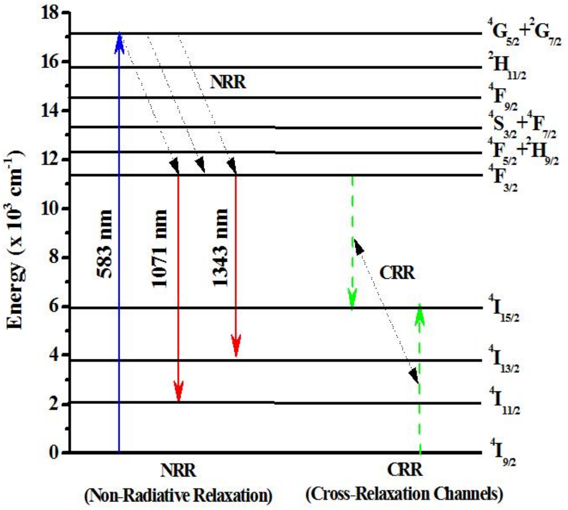

Figure 7: Energy level diagram of Nd^{3+}-doped NBB oxyfluoride glasses with exciation, emission and cross-relaxation channels.

Nd^{3+} ions in NBB oxyfluoride glasses. The absorption spectra of the samples appeared as eight peaks in the visible range and three peaks in the NIR region. The absorbance was not found to increase significantly with increasing Nd_2O_3 concentration. The transition $^4G_{5/2}+^2G_{7/2}$ exhibited the highest absorbance and it was therefore selected for use for exciting the emission of glasses. The emission spectrum of the samples was measured in the NIR range at a wavelength of 583 nm.The spectrum was found to be composed of emissions at wavelengths at 1071 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1343 nm ($^4F_{3/2} \rightarrow {}^4I_{13/2}$). The transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ is of most interest due to it's relevance as a 1.07 μm laser materials. The emission intensity was found to increase for concentrations of Nd_2O_3 up to 0.50 mol%. Beyond this it was found to decrease due to the concentration quenching effect. It was therefore concluded that 0.50 mol% of Nd_2O_3 is the optimum concentration of $Nd_2O_3$to add to sodium barium borate oxyfluoride glasses to make them suitable for use as 1.07 μm laser materials.

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