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Structural, spectroscopic and optical gain of Nd^{3+} doped fluorophosphate glasses for solid state laser application

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ABSTRACT

Nd^{3+} doped fluorophosphate glasses (PANCaFN) with chemical composition of (50-x) P_2O_5–$12Na_2O$–$8Al_2O_3$–10CaO–10KF–$10CaF_2$-xNd_2O_3 (where x = 0, 0.5, 1.0, 1.5 and 2.0 mol%) have been successfully prepared by melt-quenching method and characterized by several techniques. The optical absorption measurements exhibited signature of Nd^{3+} absorption bands in fluorophosphate glasses showed. The spectroscopic analysis have been carried out using Judd-Ofelt parameters and oscillator strength to determine radiative properties such as radiative transition probability (A_R), branching ratio (β_r), lifetime (τ), emission cross-section (σ_e) and quantum efficiency (η). The highest emission intensity was found at 1060 nm for transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ under excitation wavelength of 582 nm for PANCaFN2. The emission cross section, branching ratio and lifetime were evaluated and showed 4.92×10^{-20} cm^2, 0.7 and 200 μs, respectively. More importantly, the outstanding quantum efficiency of PANCaFN2 could reach to 98.92%. The addition of Nd^{3+} ion into fluorophosphate glass could enhance the spectroscopic properties which could play as a potential candidate for solid state applications. Theoretical optical gain evaluation and experimental calculation confirmed that PANCaFN2 had the higher gain than other samples.

1. Introduction

The utilization of glass materials as the host for neodymium (Nd^{3+}) ion was firstly introduced by Snitzer [1]. They found that stimulated emission radiation could be achieved with 2.0 wt % Nd_2O_3 doped barium crown glass by using xenon flash lamp as the pumping source. After this pioneer work, the research on glass materials as the host for rare-earth ion is intensively developed. The study for effect of amorphous glass materials is highly important in order to find the optimum composition and type of host matrix glass [2]. Nd^{3+} has been one of the most popular among the rare earth ions and attracted a lot attention of researchers on laser field since it has the great potential in wide applications. Some of its applications are optic amplifier, waveguide laser, fiber optics, and optic data storage system [3–5]. Another promising application of Nd^{3+} glass is as the optics communication at infrared (IR) wavelength range because the radiation of Nd^{3+} at energy transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is quite efficient [6,7].

The development of laser technology also have the close relationship with Nd^{3+} ion due to its ability to provide the lasing light pulse and high power [8]. The high emission cross section at energy transition of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ at wavelength of 1064 nm is one of the advantages of Nd^{3+} ion. Host glass doped with Nd^{3+} ion is an important optic material for laser amplifier. On another side, the requirements for commercial laser must have the strong fluorescence, strong absorption, and high quantum efficiency [9]. Research on spectroscopic and lasing properties of Nd^{3+} ion doped glass is interested because it can be facilely prepared [10].

As it is well-known, Nd^{3+} ion has been widely doped into several host materials such crystal [11], ceramic [12], and glass [13–16]. The advantages of using glass materials compared to the crystals are wide emission radiation, low boiling point, high dopant concentration, and more transparent [17]. Dekker et al. [18] reported that some disadvantages of crystal materials as the host materials for laser application compared to the amorphous are requirement of high flux

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temperature, relatively slow, and low quality of optic properties. Therefore, amorphous host material glass is the favorable candidate. Several host matrix glasses that have been widely used are silica [19], phosphate [20], borate [21], tellurite glass [22] and so on. The previous research stated that silica glass had several merits such as good stability, high transparency, and low coefficient thermal expansion. Furthermore, silica glass also had the low refractive index nonlinear, high surface and tensile strength [23]. However, the phosphate glass also can be a good host matrix for Nd^{3+} ion since it has good fluorescence properties, low thermal-optic and low nonlinear refractive index. Moreover, the glass phosphates also have low transition temperature, low boiling point, and high thermal expansion coefficient. Those properties provide the suitable requirements for optic fiber and waveguide laser [24,25]. In this work, we try to evaluate the spectroscopic and optical gain properties of different concentration Nd^{3+} ion doped fluorophosphate with containing several modifiers. The purpose of adding Al_2O_3 and CaO modifiers are to increase stability and overcome the volatilization, while Na_2O modifier is to enhance the homogeneity and to lower the melting point of the glass matrix.

2. Experimental section

2.1. Preparation

The raw materials (NH_4) H_2PO_4, Al_2O_3, Na_2CO_3, KF, CaO, CaF_2 and Nd_2O_3 (purity 99,9%) were used to prepare glasses. The glass sample was prepared based on chemical composition below:

(50-x) P_2O_5–$8Al_2O_3$–$12Na_2O$–10KF–10CaO–$10CaF_2$-xNd_2O_3 where x is the concentration of Nd^{3+} with variation of 0, 0.5, 1.0, 1.5 and 2.0% mol then were named as PANCaF, PANCaFN1, PANCaFN2, PANCaFN3, PANCaFN4, respectively. The glass samples were prepared by melt-quenching technique at 1200 °C followed by annealing at 500 °C for 3 h. The glass sample was cut with size of 10 ± 0.5 × 10 ± 0.5 × 3.0 ± 0.5 mm to have the optimum dimension for further characterizations. The glass also was polished to have the high transparency.

2.2. Characterizations

The structural properties were studied by X-ray diffractometer (XRD) and Fourier Transform Infrared (FTIR). The UV-3600 Shimadzu spectrophotometer was performed to record the optical spectrum and to further use for bandgap calculations. While the emission spectrum of each sample was obtained using a spectrofluorometer Quanta Master (QM-300) made by Photon Technology International (PTI)-Horiba. Based on the optical properties results, the spectroscopic parameter including oscillator strength (f), JO intensity parameters (Ω_2, Ω_4 and Ω_6), radiative transition probability, (A_R), branching ratio (β_r), lifetime (τ), emission cross-section (σ_e) and quantum efficiency (η) were determined.

3. Results and discussion

3.1. Structure properties

Fig. 1 shows the X-ray diffraction pattern of different content of Nd^{3+} doped fluorophosphate glass. No sharp crystalline peak is observed from the XRD graph suggesting that these samples have amorphous in nature. The broad peak is caused by the regular distance of inter-atomic known as short range order (SRO) between the closest molecules. The intensity of each sample is the same for different Nd^{3+} concentration which implies that Nd^{3+} concentration do not affect the diffraction pattern of Nd^{3+} doped fluorophosphate glass.

FTIR spectra was performed and recorded at wavenumber of 600–1450 cm^{-1} to get more information about the structure of Nd^{3+} doped fluorophosphate glass. It can be clearly observed from Fig. 2 that all sample have four peaks absorption located at about 719, 877, 1087, and 1240 cm^{-1}. Table 1 summarizes the assignments of each peak absorption. The broad absorption at wavenumber of 719–772 cm^{-1} was caused by symmetric vibration of bonding P–O–P which is known as $(POP)_s$. The appearance of absorption at wavenumber of 877 cm^{-1} could be assigned as asymmetric stretching of bonding P–O–P [25]. Another absorption band at 1087 cm^{-1} assigns of symmetric stretch by non-bridging oxygen effect in PO_2 group which indicates the of formation tetrahedral phosphate Q^2 [26]. The last absorption band at 1240 cm^{-1} shows the vibration asymmetric stretch between P–O in PO_2 group also known as $(PO_2)_s$. Overall, the addition of Nd^{3+} concentration did not significantly change the peak location and intensity of FTIR spectra even with the highest Nd^{3+} concentration of 2% mol due to Nd_2O_3 partly replaced the phosphate sides.

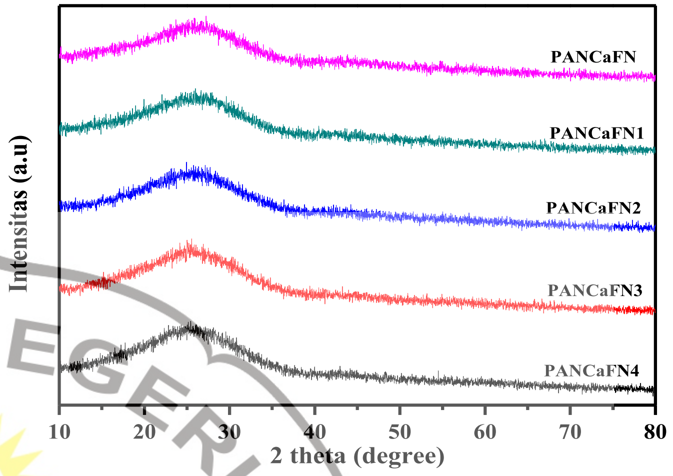

Fig. 1. X-ray diffraction pattern of different content of Nd^{3+} doped fluorophosphate glass.

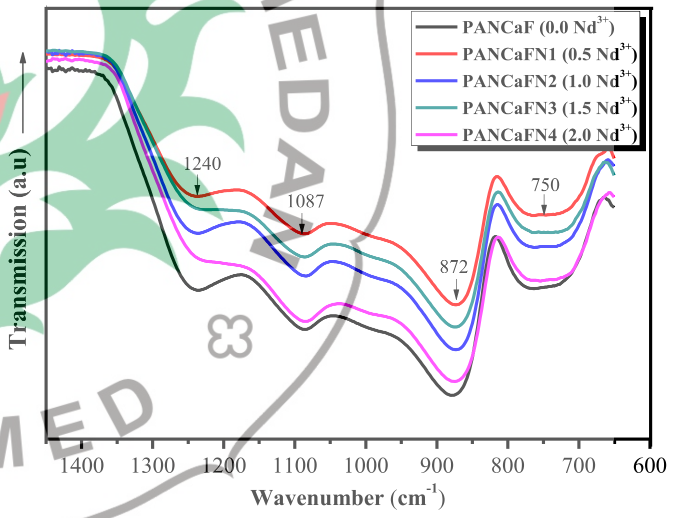

Fig. 2. FTIR of different content of Nd^{3+} doped fluorophosphate glass.

3.2. Absorption spectra

Eleven absorption peaks were observed for Nd^{3+} doped fluorophosphate glasses as shown in Fig. 3. The eleven peak absorptions at 329, 352, 430, 475, 526, 581, 629, 684, 746, 804 and 874 nm are contributed from the transition energy of $^4I_{9/2} \rightarrow {}^4D_{7/2} + {}^2I_{11/2}$, $^2D_{5/2}$, $^2P_{1/2}$, $^2G_{9/2}$, $^4G_{7/2}$, $^2G_{7/2} + {}^4G_{5/2}$,$^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$,$^4F_{5/2}$ and $^4F_{3/2}$, respectively. It is found that absorption intensity of Nd^{3+} is higher in host borate glass than in phosphate glass [27]. The absorption of Nd^{3+}

Table 1
FTIR assignments.

Wavenumber (cm^{-1})	Assignments
719–772	Symmetric stretching vibration of bonding P–O–P so-called $(POP)_s$
871–879	Asymmetric stretching vibration of P–O–P groups
1070–1150	Symmetric stretching from *non-bridging oxygen* effect of O–P–O
1240–1246	Symmetric vibration between P–O in PO_2 group so-called $(PO_2)_{as}$

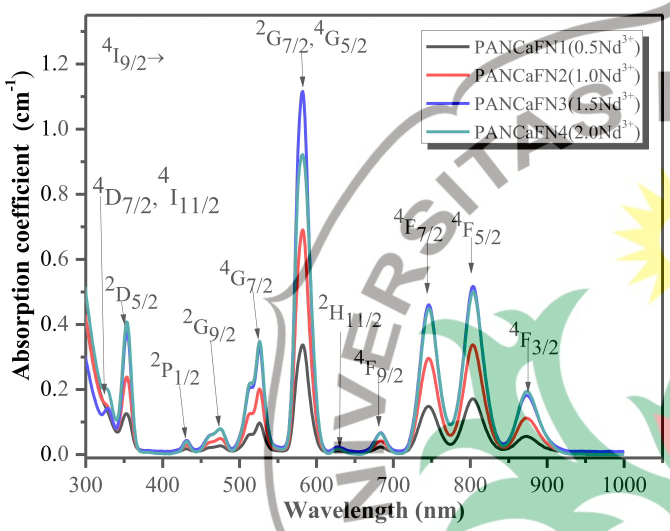

Fig. 3. Optical absorption spectra of different content of Nd^{3+} doped fluorophosphate glass.

doped fluorophosphate glass as shown in Fig. 3 where intense electron transition arise from 4f-4f [28]. From Fig. 3 can be seen that Nd^{3+} doped glass can emit light by several excitation wavelengths such as 526, 582, and 805 nm. Overall, the absorption intensity increases by adding more Nd^{3+} ion concentration. From all absorption transition emission, there is one the most sensitive peak so-called hypersensitive transition for energy transition of $^4I_{9/2}\rightarrow{}^2G_{7/2}+{}^4G_{5/2}$. It follows the selection rules $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, and $\Delta S = 0$ [29]. This transition shows highest reduced matrix element $\|U^{\lambda}\|^2$ hence this transition is important to study their oscillator strength. In this work, hypersensitive transition located at the wavelength of 582 nm with different absorption intensity for various Nd^{3+} concentration.

Fig. 4 exhibits more clearly the effect of Nd^{3+} concentration against the intensity for hypertensive transition. It is obviously observed that by increasing the Nd^{3+} concentration from 0 to 1.5% the intensity gradually elevates. However, by further increasing the Nd^{3+} concentration to 2% mol the intensity slightly decreases compared to PANCaFN3 (1.5%). This might be related to actual Nd^{3+} concentration in the glass sample as reported by other group for Nd^{3+}-doped fluoro-aluminophosphate glasses which the absorption with higher concentration of 8% mol was slight lower than 4% mol [29]. Based on this result, the optimum concentration of Nd^{3+} is 1.5% to give the highest intensity. The unique property of transition f-f has the sensitive oscillator strength against environment to cause the hypersensitive transition in host matrix Nd^{3+} doped glass [30,31]. As known that hypersensitive transitions obey the selection rule of $\Delta S = 0$, $\Delta l \leq 2$ and $\Delta J \leq 2$ to make ion lanthanide in solid materials have the stronger oscillator strength than in liquid [32–34]. It is seen that all the samples have almost the same wavelength position. Table 2 lists the experimental and calculation oscillator strength for different Nd^{3+} doped glass fluorophosphates. The maximum value of oscillator strength was obtained from the energy transition of $^2G_{7/2}+{}^4G_{5/2}$ based on formula in literature [35–37]. For comparison purpose, the other oscillator strength data from other glass phosphate is also provided [38]. From these data, it can be seen that the number of transition absorption band of this particular work is higher than other glass medium. The standard deviation oscillator strength in glass medium PANCaFN3 is ± 0.93 as the lowest among other samples.

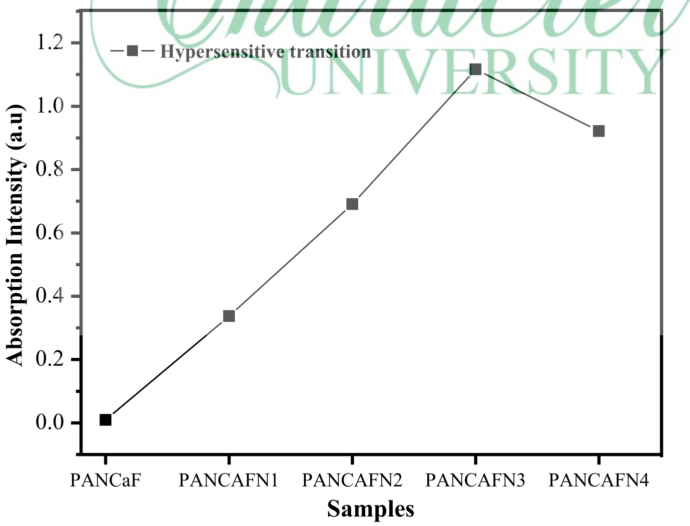

Fig. 4. Hypersensitive transition position of Nd^{3+} doped fluorophosphate glass.

Judd-Ofelt (JO) parameter that states the spectroscopic intensity of Nd^{3+} doped glass was calculated according to equation in literature [39] and listed in Table 3. Some JO parameter from the previous report also included as comparison [24,40]. The Ω_2, Ω_4 and Ω_6 parameter was obtained by using least square fitting method that can be used to predict the transition properties such as branching ratio, radiative transition probability, radiative lifetime and luminescence linewidth. Table 4 lists the Judd-Ofelt intensity parameters and quality factor of different content Nd^{3+} doped fluorophosphates. It is known that Ω_2 has a relation to covalent bonding of rare earth with oxygen in the host glass. Among of the samples, the PANCaFN2 has the highest Ω_2 value which indicates the strongest bonding of Nd^{3+} and oxygen. As shown in Table 4, the value of Ω_2 of each sample in this research is lower than value of Ω_6. The covalent bonding of Nd^{3+} doped glass is also still stronger than phosphate glass in other reports [24,40]. The relationship of Judd-Ofelt intensity parameter in this paper follows the trend of $\Omega_6 > \Omega_2 > \Omega_4$. As quality factor $\chi(\Omega_4/\Omega_6)$ is also another important properties of glass medium laser, the quality factor of sample PANCaFN4 is found to be the highest among the as-prepared sample and has the value higher than previous report for Na–K-phosphate and fluorophosphate.

Both of indirect and direct band gap of Nd^{3+} doped glass was evaluated using Tauc plot and the results are shown in Fig. 5 and Fig. 6, respectively. The plot of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ against energy were instrumental in arriving at the direct and indirect band gaps, respectively. The rare earth oxide plays a role of modifier as they tend to change in structural and optical behavior of glass. Addition of Nd_2O_3 for PANCaF1 decreases the optical direct band gap while increase in indirect band gap and then gradually increases the optical band gap up to PANCaF3. The fall in intensity beyond PANCaF3 can also be the factor behind reduction of optical band gap for PANCaF4. The Urbach energy values

Table 2
Experimental (f_{exp}) and theoretical (f_{cal}) oscillator strength values (f x 10^{-6}) of Nd^{3+} doped fluorophosphates glass.

Transition	PANCaFN1 (0.5Nd^{3+})		PANCaFN2 (1.0Nd^{3+})		PANCaFN3 (1.5Nd^{3+})		PANCaFN4 (2.0Nd^{3+})		Glass B [38]	
$^4I_{9/2}$ →	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^4D_{7/2}+{}^2I_{13/2}$	–	–	–	–	1.29	0.42	0.99	0.51	–	–
$^4D_{3/2}$	7.60	5.84	10.87	9.d23	10.65	9.23	13.15	11.47	–	–
$^2P_{1/2}$	0.68	0.52	0.69	0.87	0.74	0.89	1.04	1.13	–	–
$^2G_{9/2}.{}^4G_{11/2}$	1.74	0.53	2.24	0.76	2.08	0.72	2.88	0.86	2.87	5.21
$^4G_{7/2}$	5.14	4.08	7.78	5.71	7.58	5.59	8.19	6.63	6.48	7.98
$^2G_{7/2}+{}^4G_{5/2}$	21.41	21.46	24.82	24.93	24.60	24.70	26.67	26.75	50.78	50.66
$^2H_{11/2}$	0.14	0.21	0.18	0.28	0.20	0.25	0.29	0.30	0.28	0.43
$^4F_{9/2}$	0.57	0.75	0.79	1.03	0.81	0.92	1.04	1.09	1.52	1.57
$^4F_{7/2}$	7.74	6.45	9.44	8.80	8.31	7.78	9.86	9.16	19.84	21.19
$^4F_{5/2}$	5.68	7.13	9.36	10.13	8.70	9.35	10.38	11.21	20.94	18.98
$^4F_{3/2}$	2.29	2.29	2.76	3.59	2.76	3.56	3.77	4.41	23.98	4.71
Δf_{rms}	± 0.97		± 1.00		± 0.93		± 1.00		± 1.25	

Table 3
Judd-Ofelt intensity parameters (x 10^{-20} cm^2) and quality factor of different content Nd^{3+} doped fluorophosphates.

Glass	Ω_2	Ω_4	Ω_6	$\chi(\Omega_4/\Omega_6)$
PANCaFN1 (0.5Nd^{3+})	7.21	4.18	7.23	0.58
PANCaFN2 (1.0Nd^{3+})	7.35	6.89	9.70	0.71
PANCaFN3 (1.5Nd^{3+})	7.18	7.09	8.47	0.84
PANCaFN4 (2.0Nd^{3+})	7.18	8.91	9.91	0.90
Na–K-phosphate [24]	4.90	3.88	6.18	0.63
Fluorophosphates [40]	4.63	2.55	6.79	0.37

were evaluated and found to be 0.285, 0.404, 0.473, 0.688 and 0.559 for PANCaF, PANCaF1, PANCaF2, PANCaF3 and PANCaF4 respectively. The increase in Urbach values with increasing in Nd_2O_3 concentration (up to PANCaF3) indicates that the bond defect increases the localization of electrons, thereby increasing the donor center which tends to create non-bridging oxygens (NBOs) as Nd_2O_3 participates in structural modifications in these glasses. The dip in intensity also correlates with the decrease in Urbach energy for Nd_2O_3 beyond PANCaF3. The band gap distribution of each sample can be clearly seen in Fig. 7.

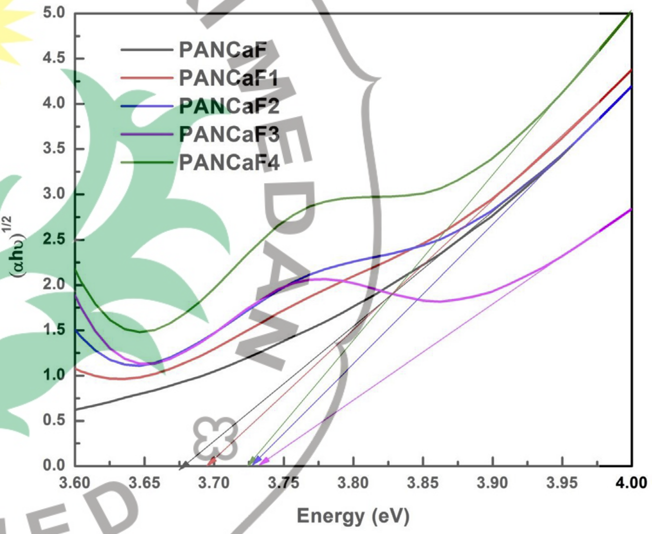

Fig. 5. Tauc plot for indirect band gap of Nd^{3+} doped fluorophosphate glass.

3.3. *Emission properties*

Emission spectra of Nd^{3+} doped glass fluorophosphate was observed under excitation wavelength of 582 nm, as shown in Fig. 8. Three transition emissions from $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ consistently appear at 902, 1060, and 1330 nm for each glass sample. Fig. 9 further shows more details the relationship between emission intensity and Nd^{3+} concentration at different peak positions (902, 1060 and 1330 nm). For emission peak at 1060 and 1330 nm, it seems when increasing the Nd^{3+} concentration from 0.5 to 1.0% the intensity significantly increases. However, with further increasing to 1.5 mol% slightly decreases and sharply drops when Nd^{3+} concentration reach to 2 mol%. This similar trend is also observable for all peak emission. The highest emission intensity at wavelength of 1060 nm was achieved by PANCaFN2.

3.4. *Radiative properties*

Table 4 reports the radiative properties of each sample including the radiative transition probability (A_R), branching ratio (β_r), and emission cross-section (σ_e). The data in Table 5 was obtained from transition of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ due to their high emission intensity. The effective bandwidth of each sample is similar about 33–36 nm and 47–54 nm for the transition energy of $4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively. It seems that concentration of Nd^{3+} did not significantly

Table 4
Radiative transition probability, (A_R), branching ratio (β_r), emission cross-section (σ_e) of Nd^{3+} doped fluorophosphate glass.

Glass	Transition $^4F_{3/2}\rightarrow$	λ_p (nm)	$\Delta\lambda_{eff}$ (nm)	A_R (s^{-1})	β_R (%)		σ_e x10^{-20} (cm^2)	$\sigma\times\Delta\lambda_{eff}$ x10^{-26} (cm^3)	$\sigma\times\tau_R$ x10^{-24} (cm^2/s)
					Exp.	Cal.			
PANCaFN1 (0. 5Nd^{3+})	$^4I_{11/2}$	1060	34.32	1793.06	0.73	0.53	3.37	0.115	4.772
	$^4I_{13/2}$	1329	48.79	387.79	0.27	0.11	1.26		
PANCaFN2 (1. 0Nd^{3+})	$^4I_{11/2}$	1060	33.22	2529.7	0.71	0.51	4.92	0.163	9.831
	$^4I_{13/2}$	1326	52.54	527.7	0.29	0.11	1.59		
PANCaFN3 (1. 5Nd^{3+})	$^4I_{11/2}$	1060	35.46	2292.63	0.74	0.50	4.18	0.148	7.092
	$^4I_{13/2}$	1330	47.78	461.01	0.26	0.10	1.55		
PANCaFN4 (2.0Nd^{3+})	$^4I_{11/2}$	1060	36.31	2722.04	0.73	0.49	4.85	0.176	7.282
	$^4I_{13/2}$	1328	54.87	537.82	0.27	0.10	1.56		
Fluorophosphates [41]	$^4I_{11/2}$	1054	28.50	1801.79	0.36	–	4.51	0.132	–

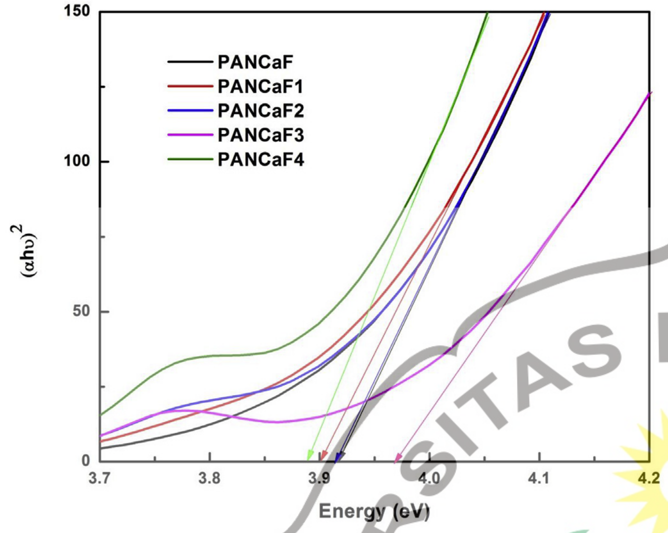

Fig. 6. Tauc plot for direct band gap of Nd^{3+} doped fluorophosphate glass.

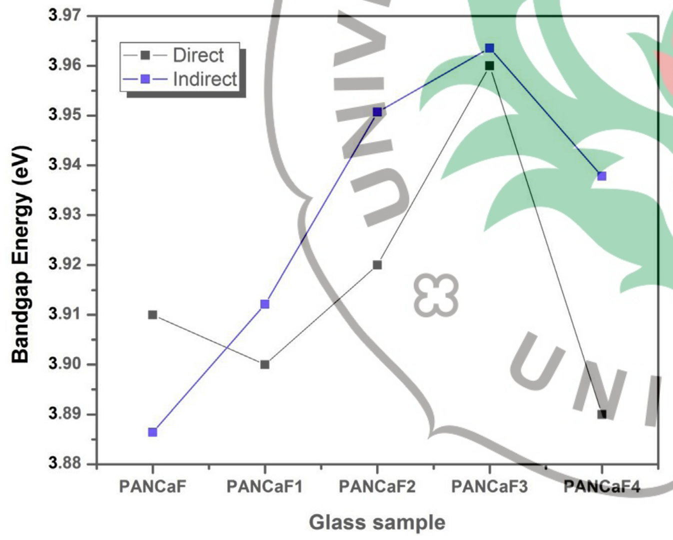

Fig. 7. Distribution of direct and indirect band gap of Nd^{3+} doped fluorophosphate glass.

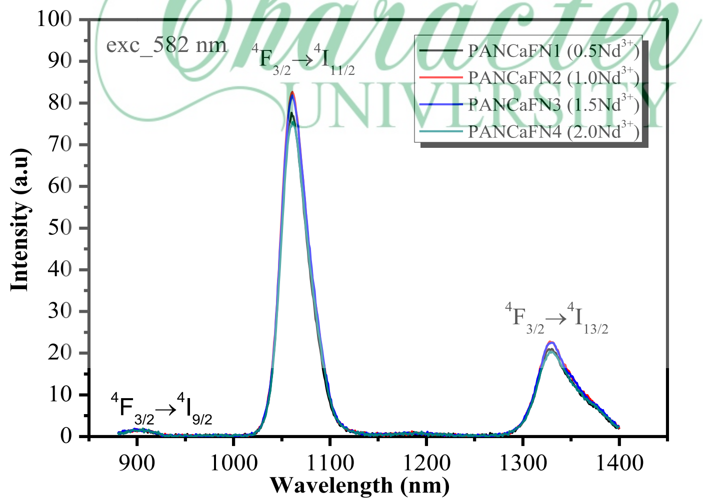

Fig. 8. Emission spectra of Nd^{3+} doped fluorophosphate glass at $\lambda_{exc} = 582$ nm.

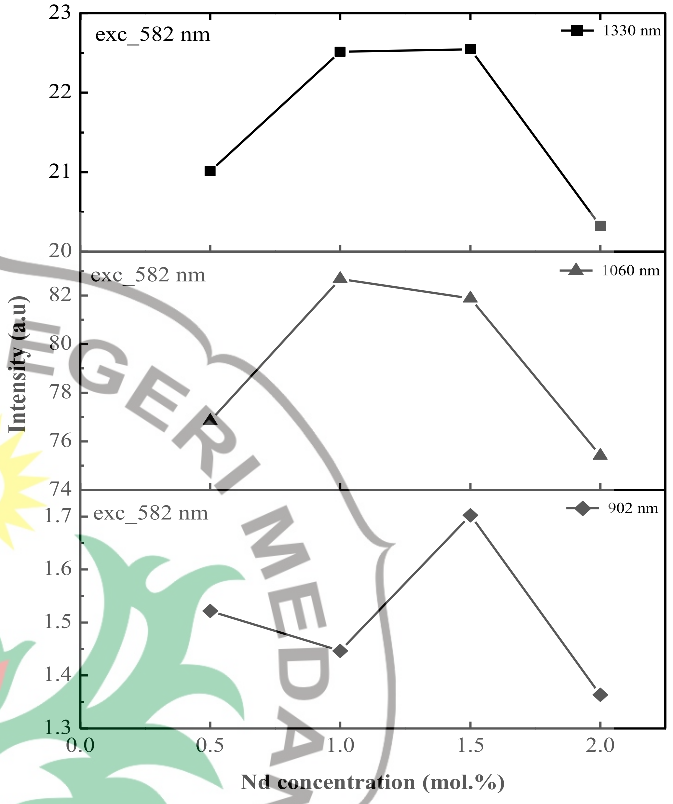

Fig. 9. Relationship between emission intensity and Nd^{3+}concentration at different emission peaks of 902 nm, 1060 nm and 1330 nm.

Table 5
Lifetime (τ) and quantum efficiency (η) of Nd^{3+} doped fluorophosphate glass.

No	Samples	τ_R (μs)	τ_{exp} (μs)	η(%)
1	PANCaFN1 (0. 5Nd^{3+})	295	141.62	48.01
2	PANCaFN2 (1. 0Nd^{3+})	202	199.82	98.92
3	PANCaFN3 (1. 5Nd^{3+})	216	169.67	78.55
4	PANCaFN4 (2. 0Nd^{3+})	179	150.15	83.88
5	Glass A [42]	320	200	62.5
6	Glass B [42]	276	180	65.2
7	PKMFAN10 [43]	491	200	41
8	PKSFAN10 [43]	326	211	65

affect the effective bandwidth. The radiative transition probability are 1793.06, 2529.7, 2292.63 and 2722.04 s^{-1} for PANCaFN1, PANCaFN2, PANCaFN3, and PANCaFN4, respectively. There is no big difference of branching ratio for different Nd^{3+} concentration. The experimental and calculation branching ratio are about 0.71–0.74% and 0.49–0.53%, respectively, for transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. However, the calculation branching ratio are about 0.26–0.29%, and 0.1–0.11%, respectively, for transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$. In this work, the experimental bracing ratio is higher than calculation. The emission cross sections are 3.37, 4.92, 4.18, and 4.85 × 10^{-20} cm^2 for PANCaFN1, PANCaFN2, PANCaFN3, and PANCaFN4, respectively. The highest and lowest emission cross section are 4.92 × 10^{-20} and 3.37 × 10^{-20} cm^2 which obtained by PANCaFN2 and PANCaFN1 glass, respectively, for transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. Our emission cross section of PANCaFN2 is slight higher than other reported data (4.51 × 10^{-20} cm^2) of fluorophosphates glass [41]. The gain bandwidth ($\sigma \times \Delta\lambda_{eff}$) and optical gain ($\sigma \times \tau_R$) parameters for the important transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ are vital information to guess the amplification of the medium in which the rare earth ions are doped. The values of gain bandwidth are 0.115 × 10^{-26}, 0.163 × 10^{-26}, 0.148 × 10^{-26} and 0.176 × 10^{-26} cm^3 for PANCaFN1, PANCaFN2, PANCaFN3 and PANCaFN4l, respectively. The optical gain values show

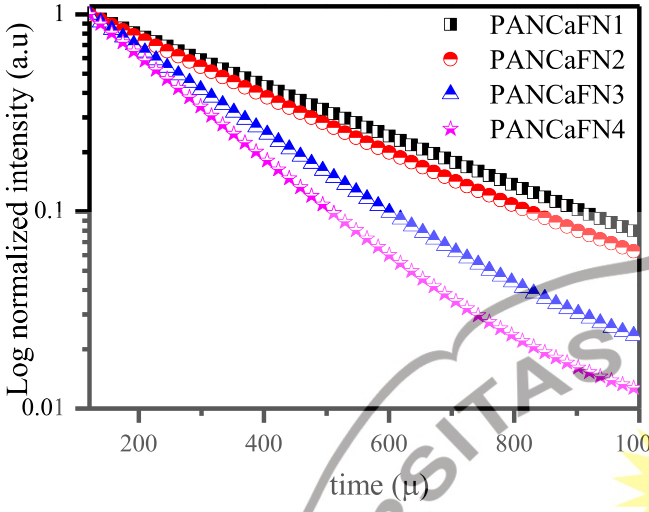

Fig. 10. Normalized decay profiles of Nd^{3+} doped fluorophosphate glass for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

4.772×10^{-24}, 9.831×10^{-24}, 7.092×10^{-24} and 7.282×10^{-24} cm^2/s for PANCaFN1, PANCaFN2, PANCaFN3 and PANCaFN4, respectively.

The normalized decay profiles of Nd^{3+} doped fluorophosphate glass was recorded at 1060 nm for transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and shown in Fig. 10. To further evaluate the luminescence radiative properties of samples, the measured lifetime values were performed under excitation of 582 nm. Table 5 shows the calculation and experimental lifetime (τ) and quantum efficiency (η) of Nd^{3+} doped fluorophosphate glass. The longest experimental lifetime of 295 μs was obtained from the PANCaFN1 and the shortest of 170 μs for PANCaFN4. However, for the longest calculation lifetime is 199.82 μs by PANCaFN2 as the closest value to experimental lifetime. This contributes to the highest quantum efficiency (98.92%) of PANCaFN2 among other sample glass. Three of as-developed Nd^{3+} doped fluorophosphate glass (PANCaFN2, PANCaFN3, and PANCaFN4) have the quantum efficiency higher than other reported works. Therefore, the sample Nd^{3+} doped fluorophosphates that developed could be a potential candidate for laser amplifier at wavelength of 1060 nm.

3.5. Optical gain of Nd^{3+} doped fluorophosphate glasses

Optical gain of samples were obtained by using Laser Diode Photopumped method [44] and displayed in Fig. 11.

Laser Diode 808 nm with *continuous wave* (CW) mode was used as

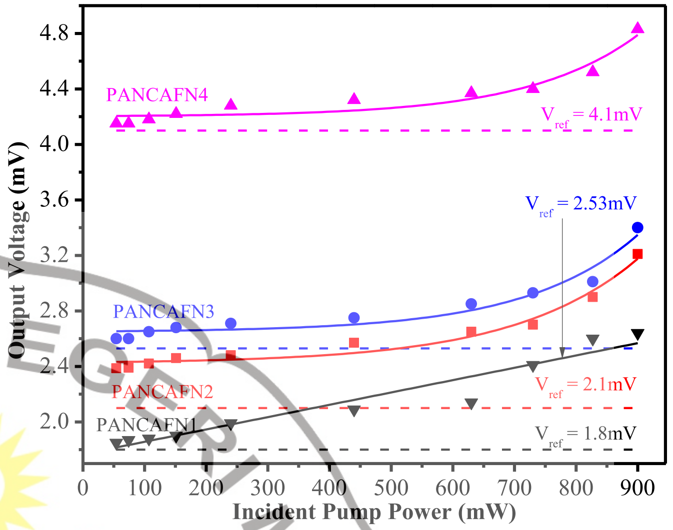

Fig. 12. Output voltage fluctuation of lasing signal from PANCaFN medium from pumped power range 54–900 mW.

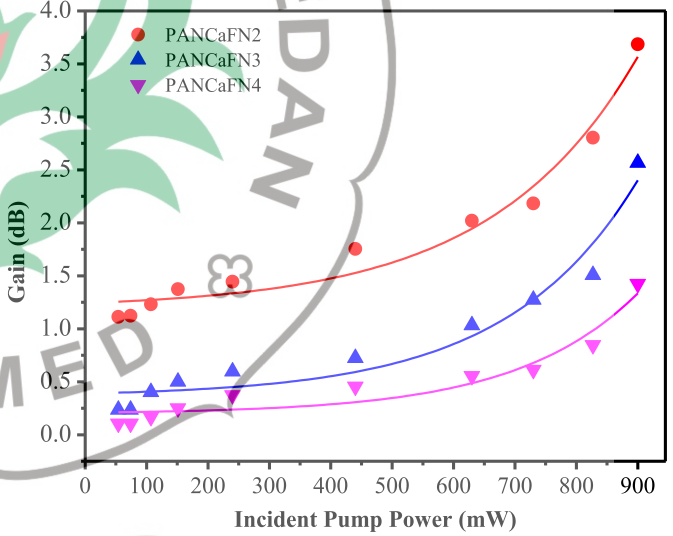

Fig. 13. Optical gain of lasing signal from PANCaFN medium from pumped power rage 54–900 mW.

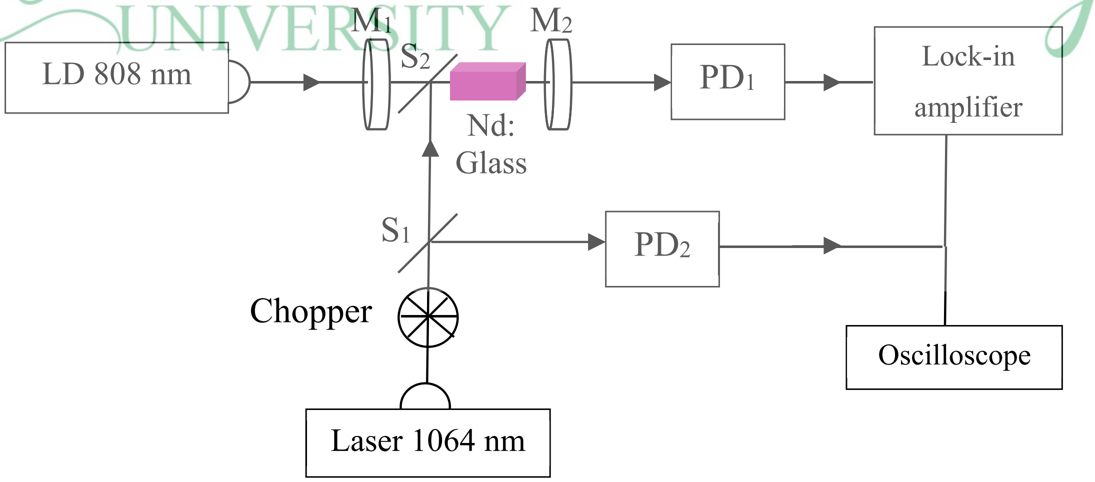

Fig. 11. Diagram of optical gain system: reference laser 1064 nm. M_1 & M_2: *mirror*, S_1 & S_2: *splitter* beam, PD_1 & PD_2: photodiode [44].

optical pumping source, whereas glasses medium based on PANCaFN were employed as laser gain medium. Output voltage of lasing signal from gain medium was measured and shown on Fig. 12. Whereas optical gain output conversion is shown on Fig. 13. Fig. 12 shows the output voltage from the integration of reference and optical gain signals for PANCaFN1, PANCaFN2, PANCaFN3 and PANCaFN4 glasses medium. The measured reference voltage is slightly different for each Nd: Phosphate medium due to the differences of glass thickness. As shown in Fig. 12 that the reference voltage for PANCaFN4 is highest than other corresponds to the PANCaFN4 thickness is thinnest compared with others. The thickness of PANCaFN1, PANCaFN2, PANCaFN3 and PANCaFN4 glasses medium is 3.34, 3.32, 3.34 and 3.31 mm, respectively.

The measured output voltage of lasing signal increases exponentially for optical pumping started from 54 to 900 mW. The maximum gain of samples is obtained from PANCaFN2 (1.0 mol% Nd^{3+}) with the increase 1.11 mV. Whereas the minimum gain is obtained from PANCaFN4 (2.0 mol% Nd^{3+}) medium with the increase 0.73 mV. The same trend was also observed for optical gain in decibel (dB). The gain value is achieved from logarithmic of measured voltage (output) with reference signal voltage. From Fig. 13 it is shown that the maximum gain is 3.69 dB for optical pump power 900 mW. The maximum gain is observed for PANCaFN2 glass for lasing signal 1064 nm as discussed in section 3.4 suggesting that such glasses could play a vital role is Q-Switch lasing materials. Moreover, the glass samples showed increasing trend with increasing pump source from 54 to 900 mW.

4. Conclusions

In summary, the Nd^{3+} doped fluorophosphates with different Nd^{3+} concentration had been successfully prepared and characterized. The glass samples had ten and eleven absorption spectra for low (< 1 mol %) and high (> 1 mol%) Nd^{3+} concentration, respectively. The strongest emission was found at 1060 nm for transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$. The Judd-Ofelt intensity parameter for all sample followed the trend of $\Omega_6 > \Omega_2 > \Omega_4$ and quality factor was comparable with elsewhere data. We also found that the optimum concentration of Nd^{3+} doped to fluorophosphate glass was 1.0 mol% (PANCaFN2) to give the highest emission intensity and radiative properties. Its emission cross section, branching ratio and lifetime were 4.92×10^{-20} cm^{2,} 0.7 and 200 µs, respectively. More importantly, the outstanding quantum efficiency of PANCaFN2 could reach to 98.92%. The optical gain value shows 9.831 $\times$ 10^{-24} cm^2/s for PANCaFN2 which correlates with the experiment demonstrated with the output gain demonstrated using diode-end-pumped laser at 1064 nm as a configuration of plane parallel resonator. The maximum gain output of 3.69 dB was achieved at the absorbed pump power of 900 mW for PANCaFN2 glass sample. All these properties of Nd^{3+} doped fluorophosphates glass might be suitable to be used for laser amplifier at wavelength of 1064 nm.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlumin.2019.116738.

References

[1] E. Snitzer, Optical maser action of Nd+ 3 in a barium crown glass, Phys. Rev. Lett. 7 (12) (1961) 444.
[2] R. Vijaya, et al., 1.06 µm laser transition characteristics of Nd3+-doped fluorophosphate glasses, Mater. Chem. Phys. 117 (1) (2009) 131–137.
[3] E. Serqueira, et al., Optical spectroscopy of Nd3+ ions in a nanostructured glass matrix, J. Lumin. 131 (7) (2011) 1401–1406.
[4] Y. Ratnakaram, D.T. Naidu, R. Chakradhar, *Absorption and emission properties of* Nd^{3+} *in lithium cesium mixed alkali borate glasses*, Solid State Commun. 136 (1) (2005) 45–50.
[5] B. Jamalaiah, et al., *Structural and luminescence properties of* Nd^{3+}*-doped* $PbO–B_2O_3–TiO_2–AlF_3$ *glass for 1.07 µm laser applications*, J. Lumin. 132 (5) (2012) 1144–1149.
[6] J. Wan, et al., Composition-dependent spectroscopic properties of Nd3+-doped tellurite–germanate glasses, Phys. B Condens. Matter 405 (8) (2010) 1958–1963.
[7] R. Jacobs, M. Weber, Dependence of the 4 F 3/2→ 4 I 11/2 induced-emission cross section for Nd 3+ on glass composition, IEEE J. Quantum Electron. 12 (2) (1976) 102–111.
[8] M. Mhareb, et al., Impact of Nd3+ ions on physical and optical properties of Lithium Magnesium Borate glass, Opt. Mater. 37 (2014) 391–397.
[9] K. Semwal, S. Bhatt, Study of Nd3+ ion as a dopant in YAG and glass laser, Int. J. Phys. 1 (1) (2013) 15–21.
[10] S. Mohan, et al., Spectroscopic investigations of Nd3+ doped flouro-and chloro-borate glasses, Spectrochim. Acta A Mol. Biomol. Spectrosc. 70 (5) (2008) 1173–1179.
[11] Y. Tai, et al., Near-infrared quantum cutting of Ce3+–Nd3+ co-doped Y3Al5O12 crystal for crystalline silicon solar cells, J. Photochem. Photobiol. A Chem. 303 (2015) 80–85.
[12] H. Yagi, T. Yanagitani, K.-I. Ueda, Nd3+: Y3Al5O12 laser ceramics: flashlamp pumped laser operation with a UV cut filter, J. Alloy. Comp. 421 (1–2) (2006) 195–199.
[13] P. Chimalawong, et al., Optical and electronic polarizability investigation of Nd3+-doped soda-lime silicate glasses, J. Phys. Chem. Solids 71 (7) (2010) 965–970.
[14] G. Gupta, et al., Influence of bismuth on structural, elastic and spectroscopic properties of Nd3+ doped Zinc-Boro-Bismuthate glasses, J. Lumin. 149 (2014) 163–169.
[15] N.G. Boetti, et al., Spectroscopic investigation of Nd3+ single doped and Eu3+/Nd3+ co-doped phosphate glass for solar pumped lasers, J. Non-Cryst. Solids 377 (2013) 100–104.
[16] K.U. Kumar, et al., Fluorescence properties of Nd3+-doped tellurite glasses, Spectrochim. Acta A Mol. Biomol. Spectrosc. 67 (3–4) (2007) 702–708.
[17] D. Murthy, et al., Investigation on luminescence properties of Nd3+ ions in alkaline-earth titanium phosphate glasses, Opt. Commun. 284 (2) (2011) 603–607.
[18] P. Dekker, et al., Continuous wave and Q-switched diode-pumped neodymium, lutetium: yttrium aluminum borate lasers, Opt. Commun. 151 (4–6) (1998) 406–412.
[19] I. Pal, et al., Fluorescence and radiative properties of Nd3+ ions doped zinc bismuth silicate glasses, J. Alloy. Comp. 587 (2014) 332–338.
[20] K. Nogata, T. Suzuki, Y. Ohishi, Quantum efficiency of Nd3+-doped phosphate glass under simulated sunlight, Opt. Mater. 35 (11) (2013) 1918–1921.
[21] B. Shanmugavelu, V. Venkatramu, V.R.K. Kumar, Optical properties of Nd3+ doped bismuth zinc borate glasses, Spectrochim. Acta A Mol. Biomol. Spectrosc. 122 (2014) 422–427.
[22] Q. Yanbo, et al., Spectroscopic properties of Nd3+-doped high silica glass prepared by sintering porous glass, J. Rare Earths 24 (6) (2006) 765–770.
[23] Q. Zhang, et al., Luminescence properties of the Eu-doped porous glass and spontaneous reduction of Eu3+ to Eu2+, J. Lumin. 129 (11) (2009) 1393–1397.
[24] M. Seshadri, et al., Spectroscopic investigations and luminescence spectra of Nd3+ and Dy3+ doped different phosphate glasses, J. Lumin. 130 (4) (2010) 536–543.
[25] B. Tiwari, et al., Preparation and characterization of phosphate glasses containing titanium, Barc Newsletter 285 (2007) 167.
[26] P.K. Jha, O. Pandey, K. Singh, FTIR spectral analysis and mechanical properties of sodium phosphate glass–ceramics, J. Mol. Struct. 1083 (2015) 278–285.
[27] J. Rajagukguk, et al., Structural and optical properties of Nd3+ doped Na2O-PbO-ZnO-Li2O-B2O3 glasses system, Key Engineering Materials, Trans Tech Publ, 2016.
[28] T. Satyanarayana, et al., Influence of crystallization on the luminescence characteristics of Pr3+ ions in PbO–Sb2O3–B2O3 glass system, J. Am. Ceram. Soc. 93 (7) (2010) 2004–2011.
[29] T.S. Gonçalves, et al., Thermo-optical spectroscopic investigation of new Nd3+-doped fluoro-aluminophosphate glasses, J. Alloy. Comp. 732 (2018) 887–893.
[30] A. Malakhovskii, et al., Magneto-optical properties of Dy 3+ in oxide glasses: the origin of the magneto-optical activity of ff transitions and its anomalous temperature dependence, Phys. Solid State 49 (4) (2007) 701–707.
[31] V. Martins, et al., Thermo-optical properties of Nd3+ doped phosphate glass determined by thermal lens and lifetime measurements, J. Lumin. 162 (2015) 104–107.
[32] S. Mohan, et al., Optical properties of alkali and alkaline-earth lead borate glasses doped with Nd 3+ Ions, Glass Phys. Chem. 34 (3) (2008) 265–273.
[33] S. Insitipong, et al., Optical and structural investigation of bismuth borate glasses doped with Dy3+, Procedia Eng. 8 (2011) 195–199.
[34] M. Zamratul, et al., Formation, structural and optical characterization of neodymium doped-zinc soda lime silica based glass, Results Phys. 6 (2016) 295–298.
[35] Y.C. Ratnakaram, A. Viswanadha Reddy, Electronic spectra and optical band gap studies in neodymium chlorophosphate glasses, J. Non-Cryst. Solids 277 (2) (2000) 142–154.
[36] C.K. Jørgensen, Absorption spectra of transition group complexes of sulphur-containing ligands, J. Inorg. Nucl. Chem. 24 (12) (1962) 1571–1585.
[37] B. Karthikeyan, S. Mohan, S.P. Jose, Preparation and characterization of Nd3+ doped sodium leadbismuthate glass, Spectrochim. Acta A Mol. Biomol. Spectrosc.

65 (5) (2006) 1134–1137.

[38] A.S. Rao, et al., Spectroscopic and optical properties of Nd3+ doped fluorine containing alkali and alkaline earth zinc-aluminophosphate optical glasses, Phys. B Condens. Matter 404 (20) (2009) 3717–3721.

[39] R.F. de Morais, E.O. Serqueira, N.O. Dantas, Effect of thermal annealing on the spectroscopic parameters of Er3+-doped sodium silicate glass, Opt. Mater. 35 (12) (2013) 2122–2127.

[40] Y. Tian, et al., Optical absorption and near infrared emissions of Nd3+ doped fluorophosphate glass, Spectrochim. Acta A Mol. Biomol. Spectrosc. 98 (2012) 355–358.

[41] K. Vijaya Kumar, A. Suresh Kumar, Spectroscopic properties of Nd3+ doped borate glasses, Opt. Mater. 35 (1) (2012) 12–17.

[42] G.A. Kumar, et al., Enhancement of optical properties of Nd3+ doped fluorophosphate glasses by alkali and alkaline earth metal co-doping, Opt. Mater. 22 (3) (2003) 201–213.

[43] R. Vijaya, et al., 1.06μm laser transition characteristics of Nd3+-doped fluorophosphate glasses, Mater. Chem. Phys. 117 (1) (2009) 131–137.

[44] J. Rajagukguk, W. Chaiphaksa, J. Kaewkhao, R. Hidayat, F. Fitrilawati, Photopumped laser diode continuous wave for optical gain determination of Nd: YVO$_4$ and Nd: YAG crystal medium, J. Met. Mater. Miner. 29 (1) (2019).