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Research Article

Switching-Concentration Effect of Li_2O and Al_2O_3 on Phosphate Glass Doped with Nd_2O_3

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ABSTRACT

The purpose of this study was to determine the switching-concentration effect of Li_2O and Al_2O_3 on phosphate glass doped with neodymium ions. The $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass was measured and analyzed for density, refractive index, absorption and near-infrared emission spectrum. The density and refractive index showed values of 2.5695 g/cm^3 and 1.5236, respectively. The optical absorption was measured and showed twelve bands in the range of 300−1500 nm. It was observed that the most intense transition $^4I_{9/2}\rightarrow{}^4G_{5/2}$ was centered at around 581 nm, which was chosen to investigate the near-infrared emission spectrum. The intense band of emission spectrum with $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition was shown in wavenumber at 9442.87 cm^{-1} (1059 nm). The Judd-Ofelt and radiative parameters were calculated and collected to support the possibility of laser application.

Keywords: Phosphate glass, Nd^{3+} ions, Optical absorption, Near-infrared luminescence, Radiative properties

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Introduction

The improved luminescence properties doped with rare-earth ions have been widely applied to UC lasers, fluorescence labeling, sensors, modern lighting, solid-state lasers, color displays and optical amplifiers [1-2]. The materials doped with RE ions were studied for luminescence through the phosphor, crystals, glass, and glass-ceramic materials. Among all materials, glass has attracted researchers' attention due to its low cost and ease of fabrication compared to crystal [3-4]. Meanwhile, the promising former glass for improved luminescence properties was phosphate glass. Phosphate glass has distinctive characteristics such as low phonon energy (~1100), high rare-earth solubility and increased luminescence quantum yield with high transparency (0.2-6 μm range) [2-7]. However, phosphate also has drawbacks such as being hygroscopic and having low chemical durability [5-7]. To improve the disadvantages, phosphates doped with alkali oxides are of great interest to some researchers [5-10]. Li_2O is one of the alkali oxides that have a lot of interest because it has benefits like improving heat-shock resistance and thermal-mechanical properties [11-12]. Lithium phosphate also has a high strong atomic bonding with a low melting point, non-hygroscopic and good Ln^{3+} solubility also contributed to the development of new materials with piezoelectric [13-14]. The composition of the glass can still be improved by adding elements such as Al_2O_3 into the glass network. It was stated by H.I. Francisco-Rodriguez et.al, that combination of lithium and aluminum in phosphate glass offers high transparency and thermal stability, making them very attractive for optoelectronic, photonic and pc-W-LEDs applications [14]. The lithium aluminum phosphate glass doped with Nd^{3+} ion has been studied and published by N. Sangwaranatee et al. with the concentration for Li_2O and Al_2O_3 of 15 and 20 mol%, respectively [7]. In his research, it was reported that the glass was successfully fabricated and displayed as transparent purple glass. Also, the glass showed greater emission intensity and good radiative properties when doped with 1.0 mol% of Nd^{3+} ions. N. Sangwaratee also stated that lithium aluminum phosphate glass-doped Nd^{3+} ions have the potential to emit a laser at 1.06 μm. This is the background of this research because this glass has the potential as a laser material medium. However, the difference is the effect of changing the concentration of Li_2O, which was previously 15 mol% to 20 mol%, and Al_2O_3, which was previously 20 mol%, to 15 mol%. The $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass was measured and analyzed for density, refractive index, absorption and near-infrared emission spectrum. The Judd-Ofelt and radiative parameter were calculated and collected to support the possibility of laser application.

Materials and Methods

The glass sample was fabricated by melt quenching technique, with a composition is $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$. The glass was mixed appropriately with high-purity chemicals (99.9%) in a sintered alumina crucible. The heating temperature was 1200 ^{0}C for 3 hours after the melts were quenched onto a stainless-steel mold. Then the glass sample was annealed to attain structural and decrease thermal stress. This process was done at the physics laboratory Universitas Negeri Medan in Indonesia. The glass has resulted transparent with purple color. The characterization of the glass sample such as density, refractive index, absorption spectrum and the near-infrared spectrum was done at the center of excellence in glass technology and materials science (CEGM) laboratory in Thailand. The density and refractive index of the sample were measured by a 4-digit sensitive microbalance (AND, HR 200) and Abbe refractometer (ATAGO) with a sodium vapor lamp as a light source (589.3 nm), respectively. The absorption spectrum was recorded on a spectrophotometer (Shimadzu, UV-3600) with a spectral resolution of 1 nm in the wavelength region of 200-2500 nm (but we just show in the range of 300-1500 nm due to other wavelengths not showing any peak). The emission spectrum was obtained by exciting the samples with 581 nm which is measured by fluorescence spectrofluorometer (Quanta Master 300, Photon Technology International with xenon lamp as excitation source).

Results and Discussion

The density (ρ), refractive index (n) and molar volume (V_m) of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass was 2.5695 g/cm^3, 1.5236 and 44.95 cm^3/mol. The results were shown lower than the previous publication by N. Sangwaranatee et al (ρ = 2.57 and n = 1.525) [7]. Based on these findings, we can conclude that lowering the Al_2O_3 concentration with the addition of Li_2O should result in a lower density and refractive index.

The absorption and emission spectrum of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass were shown in Figure 1. The glass shows twelve bands in the range of 300−1500 nm. Meanwhile, the band was assigned at 353, 431, 462, 474, 513, 526, 581, 628, 683, 746, 804 and 873 nm, which corresponds to the transition from $^4I_{9/2}$ to $^4D_{1/2}$, $^2P_{1/2}$, $^4G_{11/2}$, $^2G_{9/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$, respectively [7-9]. It is observed that the most intense transition $^4I_{9/2}\longrightarrow{}^4G_{5/2}$ is centered at around 581 nm, which is chosen to investigate the near-infrared emission spectrum. The absorption spectrum was shown to be similar to the previous work and the intensity also did not have a significant change [7]. The emission spectrum was shown in three bands that fall at 11001.10, 9442.87 and 7524.45 cm^{-1} which are assigned to $^4F_{3/2}\longrightarrow{}^4I_{9/2}$, $^4I_{11/2}$ and $^4F_{13/2}$, respectively. The intense band with $^4F_{3/2}\longrightarrow{}^4I_{11/2}$ transition was shown in wavenumber at 9442.87 cm^{-1} (1059 nm) [8-10, 15]. The transition at $^4F_{3/2}\longrightarrow{}^4I_{11/2}$ shows a slight decrease in wavelength of about 3 nm from previous publications [7]. From this, we can see that reducing the concentration, especially of metal oxide (Al_2O_3), which is replaced by alkali oxide (Li_2O), which has a low molecular weight, also has an effect on the emission spectrum. Figure 1 also shows process luminescence (excitation, emission and non-radiative) by energy level diagram.

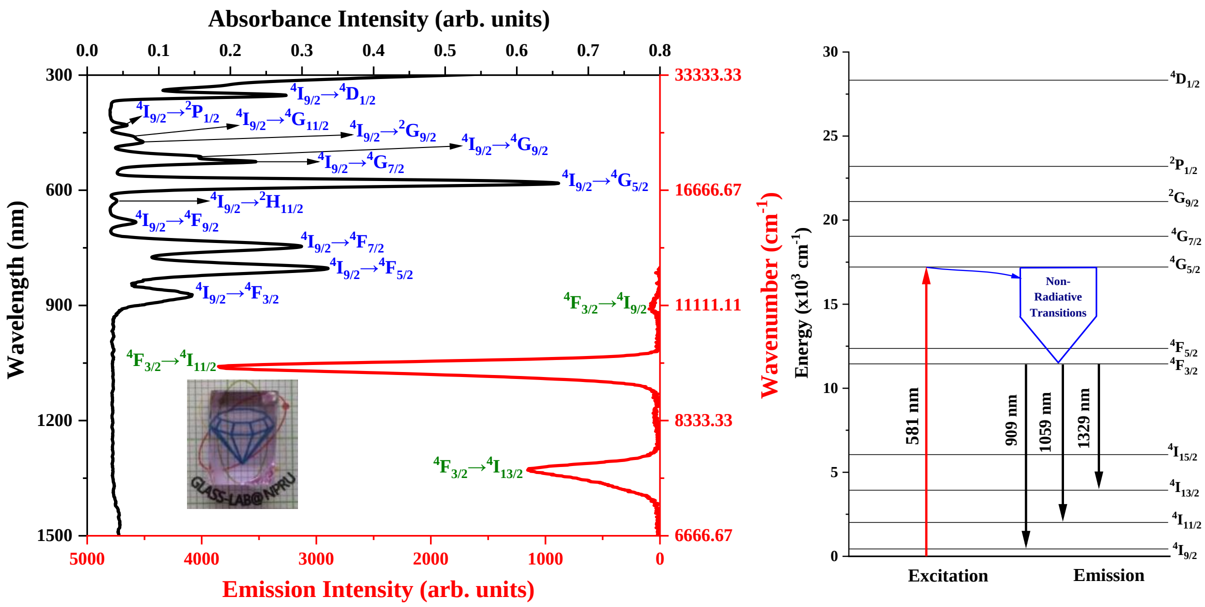

Figure 1 Absorption and Emission spectrum (left), energy level diagram (right) of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass

The decay time curve of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass was shown in Figure 2. The decay time curve of Neodymium $^4F_{3/2}$ level in the glass was studied upon 581 nm excitation performed monitoring the emission at 1059 nm ($^4F_{3/2} \longrightarrow {}^4I_{11/2}$). The decay time was fitted by an exponential and the value was169 μs. This value is used to obtain the quantum efficiency by dividing it by the radiative decay time from the J-O theory.

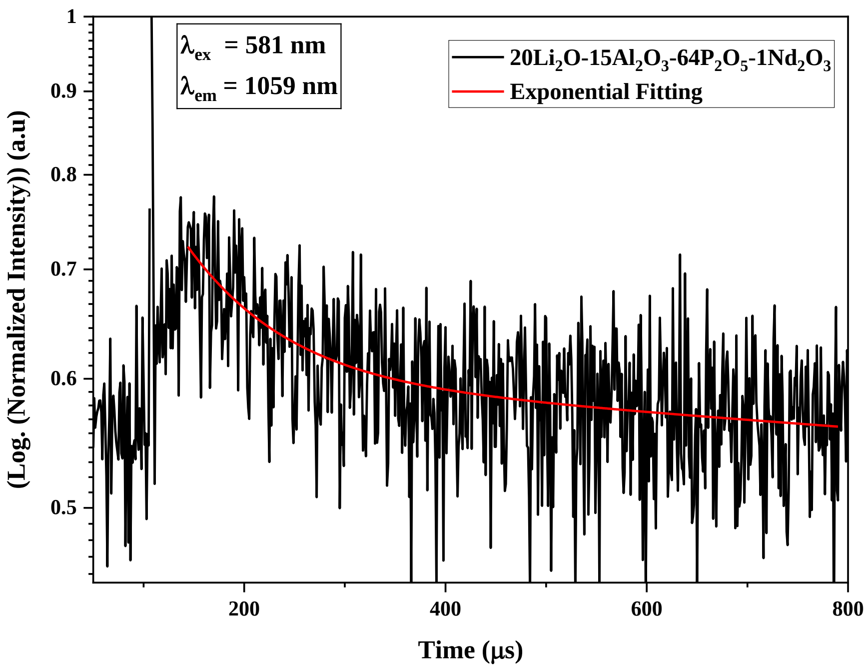

Figure 2 Decay Time analysis of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass

The intensity parameters of Judd-Ofelt (J-O) provide information about the local structure and chemical bonding between rare-earth ions and the ligand field. JO parameter also was calculated to obtain the radiative properties of the glass sample. Meanwhile, the formulation for the calculation has been previously described by N. Sarangwanatee et al [7]. The greater value of Ω_2, the greater extent of molecular orbital overlapping between Nd^{3+} and O^{2-} and thus the more covalent character. However, the higher value of Ω_4 and Ω_6 supported information about the rigidity and viscosity of the glass sample [15-17]. While the Δ_{rms} value is required to be less than 1 to know the calculation of the experimental and the calculated can be used [18]. The ratio of spectroscopic quality factor (χ) was calculated by dividing Ω_4 and Ω_6 values. The J-O parameters were shown in Table 1 with the value of oscillator strength by experimental and calculated can be trusted and used. The Ω_2, Ω_4 and Ω_6 were 4.87×10^{-20}, 2.35×10^{-20} and 7.25×10^{-20} cm^2. As shown in Table 1, the Ω_2 of the previous publication by N. Sangwaranatee et al. was lower than our publication, this can support our glass being more asymmetric and more covalent between Nd-O. But the Ω_4 was shown lower but Ω_6 was shown higher in our publication, which proves that our samples have high rigidity and viscosity of Nd^{3+} ions and ligand anions in glass samples. The highest value was Ω_6, confirming the high rigidity and viscosity of Nd^{3+} ions and ligan anions in the glass sample. The trend value was similar to the previous publication by N. Sangwaranatee et al. which is $\Omega_6>\Omega_2>\Omega_4$ [7]. The value of χ was 0.32, which is lower than in the previous publication because the concentration of Al_2O_3 decreases with the addition of Li_2O.

Table 1 J-O parameters (Ω_2, Ω_4 and Ω_6), Δ_{rms} and χ of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass

Transitions	λ_{abs} (nm)	Energy (cm^{-1})	Oscillator Strength			
			Present work		LAP: Nd1.00 [7]	
			f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^4I_{9/2}\rightarrow{}^4D_{1/2}$	353	28328.61	0.62	2.54	7.07	4.24
$^4I_{9/2}\rightarrow{}^2P_{1/2}$	431	23201.85	0.37	0.30	1.32	0.49
$^4I_{9/2}\rightarrow{}^4G_{11/2}$	462	21645.02	0.97	0.23	1.09	0.20
$^4I_{9/2}\rightarrow{}^2G_{9/2}$	474	21097.04	1.10	0.44	1.39	0.43
$^4I_{9/2}\rightarrow{}^4G_{9/2}$	513	19493.17	1.94	1.32	2.26	1.37
$^4I_{9/2}\rightarrow{}^4G_{7/2}$	526	19011.40	3.07	2.92	3.93	3.21
$^4I_{9/2}\rightarrow{}^4G_{5/2}$	581	17212.70	14.20	14.21	14.10	14.14
$^4I_{9/2}\rightarrow{}^2H_{11/2}$	628	15923.56	0.09	0.19	0.18	0.16
$^4I_{9/2}\rightarrow{}^4F_{9/2}$	683	14641.28	0.46	0.71	0.35	0.57
$^4I_{9/2}\rightarrow{}^4F_{7/2}$	746	13404.82	3.07	3.39	4.22	2.54
$^4I_{9/2}\rightarrow{}^4F_{5/2}$	804	12437.81	6.34	6.32	4.75	5.67
$^4I_{9/2}\rightarrow{}^4F_{3/2}$	873	11454.75	2.27	1.59	1.10	2.02
Δ_{rms}			0.69		1.16	
Ω_2 (x 10^{-20} cm^2)			4.87		4.19	
Ω_4 (x 10^{-20} cm^2)			2.35		3.90	
Ω_6 (x 10^{-20} cm^2)			7.25		5.41	
χ			0.32		0.72	

Moreover, the radiative properties such as radiative transition probability (A), stimulated emission cross-section (σ_e), the effective line width of the emission peak ($\Delta\lambda_{eff}$), the branching ratio experimental (β_{exp}) and calculated (β_{cal}) and the radiative lifetime (τ) by experimental and calculated. The branching ratio was used to predict the gaining stimulation emission from any particular transition and also supported laser medium application with a value should $\geq$ 0.5. The radiative lifetime is dependent on the total probability of a spontaneous transition. Table 2 was shown the transition of $^4F_{3/2}\rightarrow{}^4I_{11/2}$ has a higher value of radiative properties due to high-intensity emission. From the branching ratio value shown this glass can also be a potential laser medium application [17-19]. But the value was lower than lithium aluminum phosphate glass doped with Nd^{3+} ions which Al_2O_3 was 20% and Li_2O was 15%. The stimulated emission cross-section of the present glass was higher than in previous work [7]. Like, C. Kesavulu et al., stated that the generally stimulated emission cross-section depends on the JO intensity parameters and effective line width of the emission peak, which are affected by host glass matrices. In addition, the emission intensity of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ laser transition at 1060 nm depends only on the Ω_4 and Ω_6 parameters since of triangle rule $|J' - J| \leq \lambda \leq |J' + J|$. Whereas, the Ω_2 parameter does not have any effect on the stimulated emission cross-section of $^4F_{3/2}\rightarrow^4I_{11/2}$ emission transition of Nd^{3+} ion [20]. G. Kumar et. al also stated how the effect of Li on increasing the stimulated emission cross-section of Nd^{3+} ion in glassy materials [21]. So, it is possible that the value of the emission cross-section is acceptable. The quantum efficiency was calculated by dividing the experimental (τ_{exp}) and calculated (τ_R) radiative lifetimes then multiplying 100%. This glass has a quantum efficiency of 48.7%.

Table 2 Radiative Properties of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$ glass

Transition	λ_p	$\Delta\lambda_{eff}$	A_R	σ_e (x10^{-22})	β_{exp}	β_{cal}
Present work						
$^4F_{3/2}\rightarrow\ ^4I_{9/2}$	909	150.41	815.04	21.1	0.02	0.28
$^4F_{3/2}\rightarrow\ ^4I_{11/2}$	1059	159.94	1656.07	74.5	0.58	0.58
$^4F_{3/2}\rightarrow\ ^4I_{13/2}$	1329	230.92	386.81	29.9	0.30	0.13
τ_{exp}	169 μs					
τ_R	347 μs					
η	48.7 %					
LAP: Nd1.00 [7]						
$^4F_{3/2}\rightarrow\ ^4I_{9/2}$	908	-	28.52	0.02	0.02	0.01
$^4F_{3/2}\rightarrow\ ^4I_{11/2}$	1063	-	1209.91	1.28	0.61	0.56
$^4F_{3/2}\rightarrow\ ^4I_{13/2}$	1334	-	918.14	1.20	0.37	0.43
τ_{exp}	-					
τ_R	-					
η	-					

Conclusions

The glass sample was successfully made using a melt quenching technique with a composition of $64P_2O_5$-$20Li_2O$-$15Al_2O_3$-$1Nd_2O_3$. The density and refractive index were lower values due to lowering the Al_2O_3 concentration with the addition of Li_2O. The absorption spectrum was shown to be similar to the previous work and the intensity also did not have a significant change. The emission spectrum was shown in three bands that fall at 11001.10, 9442.87 and 7524.45 cm^{-1} which were assigned to $^4F_{3/2}\rightarrow^4I_{9/2}$, $^4I_{11/2}$ and $^4F_{13/2}$, respectively. The transition at $^4F_{3/2}\rightarrow^4I_{11/2}$ showed a slight decrease in wavelength of about 3 nm from previous publications. The emission intensity of this glass was higher than in the previous work. The decay time was fitted by an exponential and the value was 169 μs. The highest value was Ω_6, confirming the high rigidity and viscosity of Nd^{3+} ions and ligan anions in the glass sample. This glass has a quantum efficiency of 48.7%. From the branching ratio value, this glass can also be used in a potential laser medium application, but the value was lower than lithium aluminum phosphate glass doped with Nd^{3+} ions which Al_2O_3 was 20% and Li_2O was 15%. The emission cross-section of this glass sample was higher than in the previous work. It can support important parameters in the development of high-gain and low-threshold laser applications.

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