Structural and Optical Properties of Er^{3+} Doped Sodium Phosphate Glasses System for Laser Medium Candidate

Rappel Situmorang[1], Noni Syahdini[2], Abd. Hakim[3], Deo D. Panggabean[4], Juniastel Rajagukguk[5], Jakrapong Kaewkhao[6]
{nonisyahdini@mhs.unimed.ac.id[1], juniastel@unimed.ac.id[2]}

Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Indonesia[1,2,3,4,5]
Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom 73000, Thailand[6]

Abstract. Erbium (Er^{3+}) doped phosphate glasses with chemical formula x(70-x) P_2O_5 – 10 Bi_2O_3 -10 Na_2O – 10 Gd_2O_3 : x Er_2O_3(x= = 0.05 ; 0.1 ; 0.5 ; 1.0 ; 3.0 mol%) were prepared by a melted-quenching process. Glass samples are cutted to the optimum shape and size: 15 x 10 x 4 mm^3. Furthermore, glasseswere smoothed to obtain a flat surface and high transparency. The physical properties like density, molar volume, and refractive molar of the glasses have been investigated by using Archimedes principle.The absorption and emission spectra have been obtained by utilize UV-Vis-NIR spectrophotometer and PTI Thoriba Spectrofluorophotometer respectively. From the measurements could be known that an increase in the concentration of Erbium ions provides a linear relationship to density and the strength value of the glass material field. In the measurement of optical absorption there are six absorption bands which are around wavelengths 379, 488, 521, 652, 803, and 978 nm. Each in sequence corresponds to the energy level: $^4G_{11/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, dan $^4I_{11/2}$. From the calculation results, it is found that the most probabilities occur at the transition 978 nm or $^4I_{15/2}\rightarrow{}^4I_{11/2}$ on the measurements at a wavelength of 200 nm to 2500 nm so that the glass has the potential as a laser glass material.

Keywords: Optical properties, Erbium, Phosphate glasses.

1 Introduction

Glasses have a role in doping rare earth ions that can be applied in the fields of lasers, optical amplifiers, wave guides, optical fibers, and optical data storage systems. Glass Phosphate is an attractive host because it can accommodate active ions without losing their properties. In addition, Phosphate glass has other interesting properties, namely having high thermal expansion, high refractive index, low dispersion, low melting point, high electrical conductivity, and various structures to accept some cation or anion exchange (Permana, Budi, Marpaung, Sahar, & Buchori, 2016; Rajagukguk, 2017; Sdiri, Elhouichet, Barthou, & Ferid, 2012). The effect of Phosphate doped Er^{3+} concentration was used to study the cooling effect

AISTSSE 2018, October 18-19, Medan, Indonesia

DOI 10.4108/eai.18-10-2018.2287361

of concentration on luminescence performance as an evaluation of rare earth content that is most suitable for laser development (Pugliese et al., 2016).

2 Method

Chemical formula used in making glass samples Er: This phosphate is (70-x) P_2O_5 – $10Bi_2O_3$ – $10Na_2O$ – $10Gd_2O_3$ – xEr_2O_3. There are 5 samples with x = 0.05; 0.1; 0.5; 1; 3 (%mol). The material is then mixed and mashed in the alumina crucible. The material is then melted in the furnace electric at 1200 ℃ for 3 hours until it is liquid. To avoid a drastic temperature drop, the fused material is then poured into stainless steel molds on other electric furnaces at a temperature of 500 ℃ in the annealing process.

After obtaining the glass material with good transparency, the sample is then cut to a size of $15 \times 10 \times 4\text{mm}^3$to obtain the optimum dimensions in measuring the physical and optical properties of the glass material. The samples that have been cut are then polished to obtain a flat surface and high transparency. The polished glass has an average thickness of 0.413 cm.

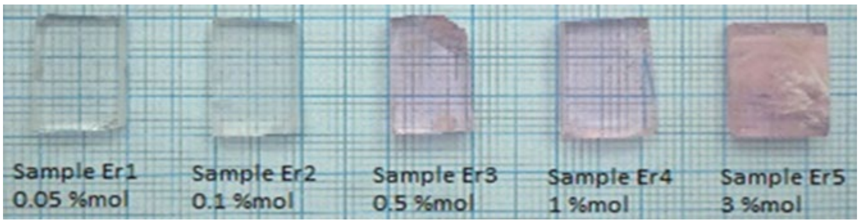

Fig. 1. Medium glass after the process of forming size and smoothing

3 Results

In Figure 1 there is a color change in the five samples which shows each difference in Er3+ ion concentration. The color change of the glass shows a pink color that matches the color characteristics of the Erbium ion.

The sample with an ion concentration of 3 %mol appears to have a darker color than the other glass because the number of Er3+ ions that occupy the glass host is tighter. Also seen at a concentration of 3 %mol of glass composition material which results in the glass not having good transparency, because the furnace process and the glass material do not melt completely.

Physical properties observed in this study are: density, molar volume, refractive index, ion concentration and polar radius. Molar density and volume are obtained from measurements using Archimedes principles. Table 1 shows the parameters of the physical properties of glass Er: Phosphate. From these measurements it can be seen that the value of Erbium ion concentration has a linear relationship to the density and field strength values of glass material.

Glass density is considered an important property for controlling glass quality. Changes in glass density are directly affected by differences in glass composition. These changes affect the structure of the glass tissue. Figure 2 shows an increase in glass density from a concentration of 0.05 to 3 %mol, this is due to an increase in the inter atomic average distance followed by the greater concentration of Er^{3+} ions inserted into the glass structure.

Table 1. Measurement results and calculation of physical properties of glass material (70-x)P_2O_5-10Bi_2O_3-10Na_2O-10Gd_2O_3-xEr_2O_3.

Parameter	Inisial Gelas Er:Fosfat				
	Er1	Er2	Er3	Er4	Er5
Molar mass	188.53	188.65	188.61	190.81	195.62
Density (g/cm^3)	3.57	3.59	3.62	3.63	3.76
Molar volume (cm^3/mol)	52.87	52.59	52.36	52.51	52.07
Ion concentration of Er3+ (N x 1022 /cm^2)	0.06	0.12	0.58	1.15	3.47
Polaron radius (Å)	1.04	0.83	0.39	0.39	0.27
Ions distance (Å)	2.57	2.04	1.20	0.96	0.66
Field strength (F x 10^{17} cm^2)	6.07	19.26	279.45	881.48	5490.68
Refractive index	1.66	1.66	1.66	1.62	1.63
Dielectric constant (ε)	2.74	2.74	2.74	2.62	2.65
Molar refraction, Rm (cm^{-3})	224.94	206.51	213.70	208.58	206.95
Electrical susceptibility, χ	0.05	0.05	0.05	0.05	0.05
Reflection loss, R(%)	29.45	27.08	28.02	26.06	26.09
Polarization of oxide ions (αm x 10^{-24} cm^3)	0.89	0.82	0.85	0.83	0.82

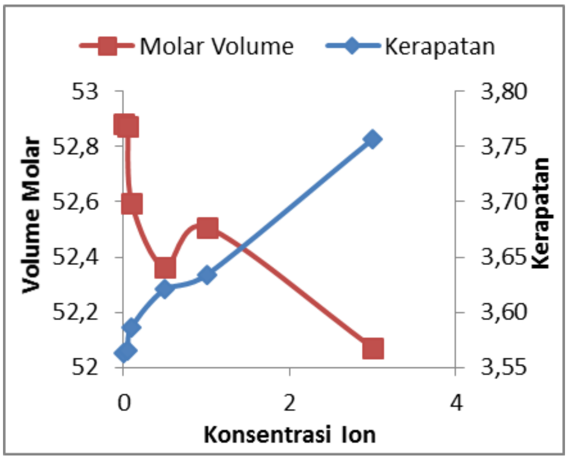

Fig. 2. Graph of density and molar volume of glass material Er: Phosphate

The ions from Er3+ that enter the phosphate tissue cause a rearrangement of the atomic structure. The properties possessed by glass network structures when there is a role for the modifying element in glass tissue that causes a decline in molar volume or decrease when the modifier's molecular weight is increased.

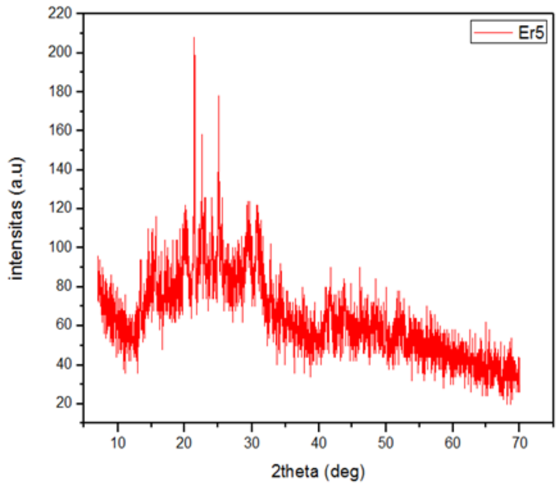

Fig. 3.XRD spectrum of glass material Er: Phosphate with a concentration of 3 %mol.

Glass X-ray diffraction spectrum Er: Phosphate is shown in Figure 3. The glass spectrum pattern shows a sharp peak in the diffraction angle (2ɵ) observation area, at a diffraction angle of 21.46o for Er5 or a glass material with a concentration of 3 mol%. The sharp peak that occurs indicates that there is a crystal characteristic in the glass material so that it can be stated that the glass is not amorphous. The shape of the mound that has a sharp peak is the result of the irregular atomic distance between the closest glass molecules.

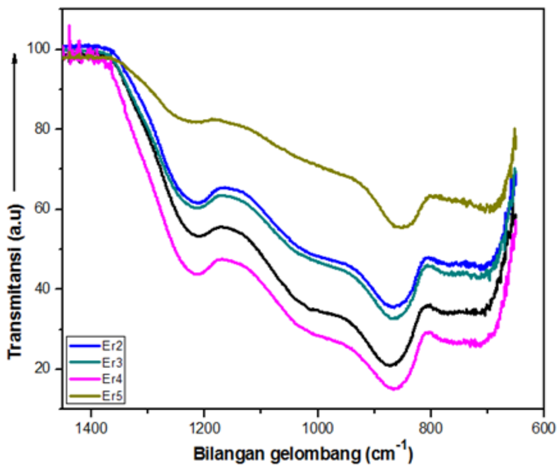

Fig. 4.FTIR spectra of glass material Er: Phosphate

In this study we can see two peaks that appear in the absorption band area of 600-1400 cm^{-1}in Figure 4. Both of these peaks are peak spectral positions that are not shifted. Both peaks were identified in this band at around 865 and 1212 cm^{-1}. Then at the top of the absorption band 865 $cm^{-1}$is associated with a different high intensity and in accordance with the harmonic vibration mode/ deformation P-O-P of PO^{-}. The peak increases with increasing vibration symmetrical intensity stretching P-O-P to Q^2 units. Whereas the 1212 cm^{-1}absorption band is associated with stretching asymmetric PO_4 groups(Maheswari et al., 2018).

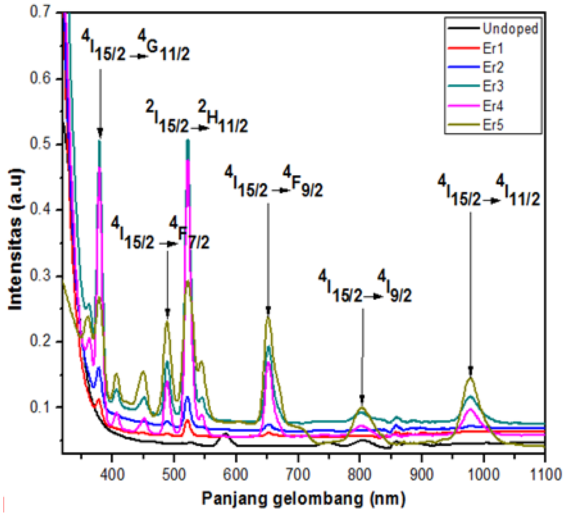

Fig. 5. Spectrum absorption glass measured by Shimadzu 3600 NIR UV-VIS

Used Shimadzu 3600 NIR UV-VIS Spectrometer for measuring glass sample absorption spectrum. Measurements were made at wavelengths of 200 nm to 2500 nm with a range of wavelength increases of 0.1 nm. The glass absorption spectrum is shown in Figure 5 in the wavelength region 320 nm to 1100 nm. From these glass samples there are six peaks which are around wavelengths 379, 488, 521, 652, 803, and 978 nm. Each sequentially corresponds to energy levels: $^4G_{11/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, dan $^4I_{11/2}$. This energy level will make it easier to explain the process of transition between energy levels. It is known that Er^{3+} ions work in wavelength regions around 1550 nm ($^4I_{13/2}\rightarrow{}^4I_{15/2}$) and 980 nm ($^4I_{11/2}\rightarrow{}^4I_{13/2}$) for telecommunications applications that are useful as optical amplifiers (Susanto, 2012).

The energy level for each transition from each glass Er: Phosphate is shown in Table 2. In the table it appears that most of the same glass transition is in the same wavelength position. During the $^4I_{15/2}\rightarrow{}^4G_{9/2}$ and $^4I_{15/2}\rightarrow{}^4G_{11/2}$ transitions that have different wavelength positions for the Er1 and Er4 glass medium, which will also affect the energy level. The difference in the position of the wavelength arises from the partial expansion of the skin caused by the shift of the charge from the ligand to the nucleus of the ion center (nephelauxetic effect) which can directly affect the molar volume of the glass medium (Rajagukguk, 2017).

In Table 3 the oscillator strength value of the glass Er: Phosphate. The standard deviation (Δf_{rms}) of the oscillator strength in this study shows the best value in the Er5 glass medium with a concentration of 3 %mol is ± 0.19. The smaller the strength of the oscillator produced by the glass medium, the better the glass produced, which affects the optical quality of the medium. The position of the absorption band and the level of energy produced by a glass are related to the strength value of the medium oscillator. Where the Judd Ofelt Analysis is used to determine the strength of the glass medium oscillator Er: Phosphate.

Calculation of transition parameters is done using Judd Ofelt analysis and line strength calculation with equations.

$$f_{meas} = \frac{3ch(2J+1)}{8m^2e^2N}\frac{9n}{(n^2+2)^2}\frac{2.3}{\bar{\lambda}}\int_{J\to J'} OD(\lambda)d\lambda$$

Where J and J' are the total angular moments of quantum numbers, $\bar{\lambda}$is the average wavelength of the absorption, *n* is the refractive index of the glass, *c* is the speed of light, *e* is the electron charge, *h* is the plank constant, *N* is the number of Er^{3+} ions, *t* is glass thickness, and OD is optical density.

Table 3. The value of oscillator strength (f x10-6) glass Er: Phosphate

Transition	Er1		Er2		Er3		Er4		Er5	
$^4I_{15/2}\rightarrow$	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^4G_{9/2}$	-	7.38	-	5.57	1.72	1.93	7.91	7.96	4.72	4.57
$^4G_{11/2}$	1.77	3.75	1.43	4.41	3.32	1.88	1.66	9.46	1.85	8.21
$^2H_{9/2}$	-	1.43	-	2.00	2.02	8.63	9.32	4.41	4.36	3.67
$^4F_{5/2}$	-	2.27	-	3.17	2.21	1.37	7.70	6.98	9.71	5.83
$^4F_{7/2}$	1.39	1.20	3.30	1.18	5.08	5.00	3.02	2.45	1.35	2.24
$^2H_{11/2}$	1.06	3.97	8.03	3.00	2.62	1.04	1.08	4.33	2.09	2.48
$^4S_{3/2}$	-	1.86	-	2.60	1.12	1.12	3.45	5.74	1.42	4.78
$^4F_{9/2}$	1.73	2.00	1.10	1.43	5.88	5.92	2.00	2.75	1.84	2.83
$^4I_{9/2}$	7.03	4.46	-	2.65	8.56	1.08	4.75	4.78	5.33	5.40
$^4I_{11/2}$	-	2.34	-	2.99	1.81	1.25	8.41	6.21	7.99	4.83
$^4I_{13/2}$	-	6.03	-	7.03	1.59	3.00	8.04	1.50	3.19	1.28
Δf_{rms}	±6.04		±4.81		±1.18		±0.56		±0.19	

The Judd Ofelt parameter which states the spectroscopic intensity for er: phosphate samples is shown in Table 4. The values of each Ω in this study have not been consistent to increase. But the covalence bond produced by the glass of er: phosphate is smaller than previous studies (Susanto, 2012). The relationship between ω produced for glass medium in this study was to follow the pattern $\Omega_2 > \Omega_4 > \Omega_6$.

Table 4. Parameters Ω_2, Ω_4, Ω_6(x10^{-20} cm^2)for Er^{3+} ions

Glass	Ω_2	Ω_4	Ω_6	$\chi(\Omega_4/\Omega_6)$
Er1	1.63	1.99	4.47	0.45
Er2	1.38	1.16	6.24	0.19
Er3	4.38	4.71	2.70	1.75
Er4	1.76	2.14	1.42	1.51
Er5	2.47	2.44	1.18	2.07

In Figure 6 shows the changes in the edge edge of optical absorption and baseline position of the glass medium spectrum can affect the energy band gap value. The Er3 chart has a higher absorption band width. This causes the value of the medium band energy gap for indirect transition to be greater than the other samples, is 3.25 eV.

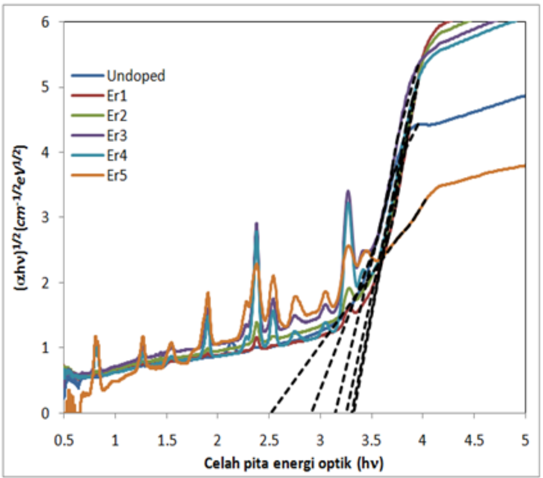

Fig. 6. Energy band gap of indirect glass Er: Phosphate

For the direct transition shown in Figure 7, the Er3 glass medium also produces a higher absorption band gap than the other glass, which is 3.5 eV. but large Eg the average for indirect transition is greater than the direct transition. This is because the baseline spectrum of indirect transitions is lower than the indirect transition.

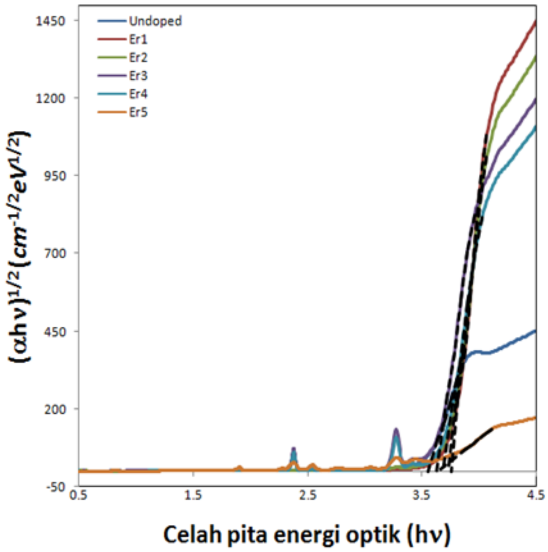

Fig. 7. Energy band gap of direct glass Er: Phosphate.

To see the suitability of the absorption spectrum that has been obtained, monitoring of the glass excitation spectrum is carried out Er: Phosphate. Figure 8 shows the Er5 excitation spectrum monitored using a 1543 nm emission wavelength. Overall, the emission spectrum produced by all of Er:Phosphate has the same pattern and excitation area.

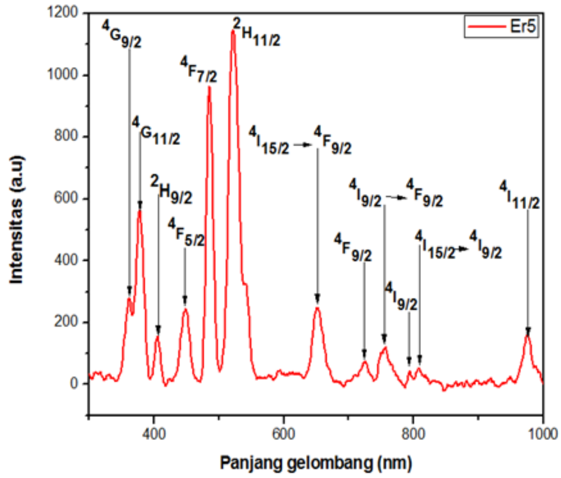

Fig. 8. Er5 glass excitation spectrum with a concentration of 3 %mol and λ_{em} is 1543 nm

There are twelve wavelength regions that can be used to excite active ions in the glass medium as shown in Figure 8. The hypersensitive transition $^2H_{11/2}$in the glass is at a wavelength of 521 nm. Drastically increased excitation band intensity was obtained at $^4F_{7/2}$at the peak of the 488 nm wave. This indicates that the correlation between 488 nm excitation wavelength and 1543 nm emission spectrum is very strong.

Figure 10 shows Er: Phosphate glass emission spectrum which is excited by light with a wavelength of 488 nm. The emission spectrum produced by the glass Er: Phosphate has a peak of $^4I_{13/2}$which is 1543 nm. Transition of the emission band can be consistently produced by each type of glass. The emission value in the approaching infrared range produces the maximum intensity. So it can be stated that the glass medium is Er: This phosphate is very potential to be used as a laser material of 1543 nm wavelength.

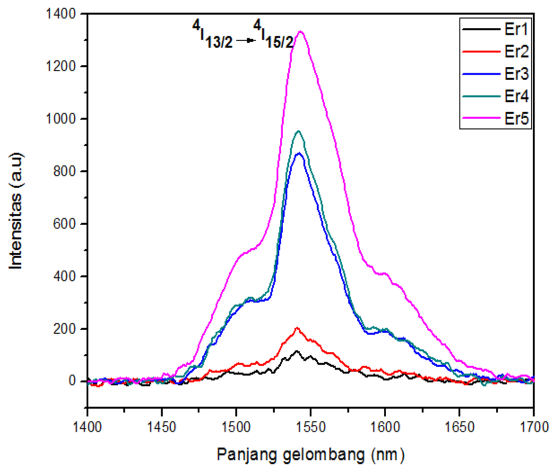

Fig. 9. Glass emission spectrum Er: Phosphate

The $^4F_{3/2}\rightarrow{}^4I_{13/2}$transition type whose peak is at a wavelength of 1545 nm is the most active luminescence among the other transitions observed in the Er^{3+} ion. So that the glass medium doped by Er^{3+} ion has the potential to be used as a laser producer in the 1545 nm waveform. This result is also supported by the highest probability value of radiation transition (A_R) for the $^4F_{3/2}\rightarrow{}^4I_{13/2}$transition in each glass. as for the large latitude of stimulated emission (σ_e) in the glass medium Er: Phosphate gets smaller with the increasing Er^{3+} ion. The biggest σ_e value is produced by Er1 medium while the lowest is obtained by Er5 medium. The magnitude of the σ_e value is influenced by the radiative transition probability (A_R) and the effective line width ($\Delta\lambda eff$) of light fluorosence.

Table 5. Wavelength of emission peak λp (nm), effective line width $\Delta\lambda_{eff}$ (nm), stimulated latitude σ_e (λ_p x10^{-20}) (cm^2), branching ratio β_R (%), probability of A_R radiation transition (s^{-1}) glass system Er: Phosphate

Gelas	Transisi	λ_p (nm)	$\Delta\lambda_{eff}$ (nm)	A_R (s^{-1})	β_R(%)		σ_e (λ_p x10^{-20}) (cm^2)
					Exp.	Cal.	
Er1	$^4I_{13/2}$	1545	74.8751	251.08	0.2154	1	9.7813
Er2	$^4I_{13/2}$	1544	78.0426	20.02	0.2124	1	7.4633
Er3	$^4I_{13/2}$	1542	74.8751	251.08	0.2048	1	5.1612
Er4	$^4I_{13/2}$	1542	73.8131	10.14	0.2063	1	3.9760
Er5	$^4I_{13/2}$	1543	74.3598	9.96	0.2048	1	3.8868

Table 6. Lifetime value in theory τ_R (μs) glass system Er: Phosphate

Glass	τ_R (μs)
Er1	3982
Er2	49947
Er3	75390
Er4	98653
Er5	100446

Radiative lifetime represents a mean effectiveness through levels between states in the environment around Er^{3+} ions. Table 6 shows the lifetime value in theory. In this study, the measurement of lifetime lifetime values could not be produced due to poor medium glass conditions for luminescence processes. Lifetime at $^4I_{13/2}$transition shows an increasing trend in glass that has a low A_R

4 Conclusions

Development of optical and laser-based optical fields in glass materials is currently being studied and studied. In this study the manufacture of glass laser medium with active Er^{3+} ion was applied in the range of near infrared surgery.

By using the composition (70-x)P_2O_5 – $10Bi_2O_3$ – $10Na_2O$ – $10Gd_2O_3$ doped with active ion xEr2O3 where x = 0.05; 0.1; 0.5; 1; 3 (%mol) can be fabricated into glass with the melt-quenching method with a high level of transparency. Through measurements and calculations performed, several physical properties and structures such as refractive index, density, field strength, infrared absorption properties and crystal bonds in glass. The addition of Erbium ions provides a linear relationship with density, ion concentration, and field strength.

There are six transitions and the top position of the glass medium absorption band Er: Phosphate occurs at 379, 488, 521, 652, 803, and 978 nm, where each energy level corresponds to: $^4G_{11/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4I_{9/2}$, dan $^4I_{11/2}$. The greatest absorption probability occurs at a wavelength of 978 nm or $^4I_{15/2}{\rightarrow}^4I_{11/2}$ with a wavelength range of 320 nm to 1100 nm. 4. The emission spectrum obtained produces emissions at the infrared wavelength of 1543 nm or $^4I_{13/2}{\rightarrow}^4I_{15/2}$.

The lifetime value obtained based on Judd Ofelt calculations on the Er: Phosphate glass system is increasing according to the increase in glass concentration value. Where the lifetime τ_R (μs) values are 3982, 49947, 75390, and 100446. Lifetime at $^4I_{13/2}$transition shows an increasing trend in glass that has a low A_R. This effect reinforces that the concentration of quenching is between glasses that have almost the same lifetime and quantum efficiency.

Acknowledgements. This work is supported by Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Thailand and grant Penelitian Unggulan Strategis Nasional (PUSNAS) from Directorate of Higher Education, Ministry of National Education, Indonesia.

References

[1]Maheswari, T., Basavapoornima, C., Linganna, K., Ju, S., Han, W.-T., & Jayasankar, C. (2018). Structural and spectroscopic properties of γ-ray irradiated Er 3+-doped lead phosphate glasses. *Journal of Luminescence*.

[2]Permana, I., Budi, E., Marpaung, M. A., Sahar, M. R., & Buchori, P. A. (2016). KARAKTERISASI SIFAT FISIK DAN ABSORPSI OPTIKAL SISTEM KACA ZnO–MgO-P2O5 MENGGUNAKAN TEKNIK MELT QUENCHING. *Spektra: Jurnal Fisika dan Aplikasinya, 1*(1), 61-68.

[3]Pugliese, D., Boetti, N. G., Lousteau, J., Ceci-Ginistrelli, E., Bertone, E., Geobaldo, F., & Milanese, D. (2016). Concentration quenching in an Er-doped phosphate glass for compact optical lasers and amplifiers. *Journal of Alloys and Compounds, 657*, 678-683.

[4]Rajagukguk, J. (2017). Preparasi, Sifat Fisis Dan Analisis Termal Medium Gelas Fluorofosfat Didoping Oleh Ion Nd3+ Untuk Aplikasi Medium Penguat Laser. *EINSTEIN, 4*(3).

[5]Sdiri, N., Elhouichet, H., Barthou, C., & Ferid, M. (2012). Spectroscopic properties of Er3+ and Yb3+ doped phosphate–borate glasses. *Journal of Molecular Structure, 1010*, 85-90.

[6] Susanto, R., (2012), *Sifat Optik Kaca Telurium Oxide yang Terdadah Ion Erbium untuk Optical Amplifier*, Tesis, Program Ilmu Fisika, Program Pasca Sarjana, Universitas Sebelas Maret Surakarta, Surakarta.