EINSTEIN (e-Journal)
Jurnal Hasil Penelitian Bidang Fisika
Available online http://jurnal.unimed.ac.id/2012/index.php/einsten
e-issn: 2407 – 747x, p-issn 2338 – 1981

PHOTOLUMINESCENCE PROPERTIES OF TB^{3+} DOPED ON PHOSPHATE GLASS MEDIUM BY ADDITION OF FLUORIDE COMPOUNDS

Elyzabeth Simanullang[1], Juniar Hutahean[1], Chayani S. Sarumaha[2], and Juniastel Rajagukguk[1]
[1]Department of Physics, Faculty of Mathematics and Natural Science, Medan State University
[2]Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University, Nakhon Pathom 7300, Thailand
elisasbetmanullang88@gmail.com

Submit: August 2024. Approved: September 2024. Published: October 2024.

ABSTRACT

Research has been conducted on the effect of the addition of fluoride compounds on the photoluminescence properties of Tb^{3+} doped on phosphate glass has been found. with the composition of glass samples are 69 P_2O_5 - 20 LiO_2 - 10 AlF_3 - 1Tb_2O_3 (P-Tb1), 59 P_2O_5 - 20 LiO_2 - 10 AlF_3 - 10 NaF - 1 Tb_2O_3 (P-Tb2) and 49 P_2O_5 - 20 LiO_2 - 10 AlF_3 - 10 NaF -10KF - 1 Tb_2O_3 (P-Tb3). All chemical compounds are in powder form with a total mass of 15 grams using the melt-qunching technique at 1100^0C. To determine the quality of the material, measurements and calculations were made of physical properties including molar mass, density, molar volume, refractive index, Tb^{3+} ion concentration, Polaron radius, molar refractivity, reflection loss and dielectric constant. Characterizations carried out include FTIR, UV-VIS-NIR Spectrophotometer, Abbe Refractometer, Spectrofluorophotometer. To study the physical properties, the optical properties were examined through their absorption and luminescence spectra. The luminescence spectrum is known by photoluminescence. Characteristic luminescence bands corresponding to electronic transitions of terbium ions were detected under two direct excitations of Tb^{3+} ions. After 377 nm excitation, the glass sample obtained terbium $^5D_4 \rightarrow {}^7F_5$ transition at 544 nm indicating green laser. The application of green laser has been investigated with CIE coordinate diagram.

Keywords: Glass Medium, Tb^{3+} Ion, Melt-quenching, characterization

INTRODUCTION

The development of glass medium research is currently of great interest to researchers because it brings new developments to the times where there are many applications in the fields of lasers, waveguides, telecommunications and others. In recent years, glasses doped with rare earth ions have played an important role in the development of modern optical technology that produces laser sources, optical amplifiers, and 3D display devices (Djamal et al., 2016). The rare earth elements are ions of the lanthanide group on the periodic table of elements research on rare earth ions is very much done in the last few decades.

Nowadays rare earth ions in glass structures have been widely used with respect to their physical, structural, thermal, electrical and optical properties. The rare earth ions doped with glass medium are an interesting subject to study for example applications such as in the fields of optoelectronics, photonics and quantum electrodynamics. Glass is a suitable material to replace crystal as the host of gain media. The disadvantages of solid crystal materials are the long and complicated growth process, expensive production costs, and the high melting point which reaches 1500^{0}C, glass doped with rare earth ions can be well developed as a luminescent material for emission efficiency (Rajagukguk et al., 2016). Rare earth metals play an important role in luminescence technology, the spectroscopic properties of rare earth ion materials depend on emission efficiency and have emission stability in the visible light to near infrared region (Ramteke et al., 2017).

Phosphate glass is one of the important materials as a glass former because it has unique properties such as low melting point, high chemical resistance, high thermal stability, low refractive index, low optical dispersion, high transparency, and good transmission in the UV-VIS-NIR region (Rajagukguk et al., 2021). Compared to silica and borate glasses, phosphate glasses have a relatively lower melting point (Rajagukguk J et al. 2022). Phosphate glass is one of the materials that has many benefits when added with modifiers made from rare earth metal oxides.

Phosphates have relatively high hygroscopicity, hence the addition of modifiers to reduce their hygroscopic properties (Altaf. M., 2010). Addition of metal oxides into phosphate glass medium such as Lithium Oxide (Li2O) gives strong chemical resistance, lowers the melting point (Rajagukguk et al., 2021). The addition of Sodium Oxide (Na2O) as a modifier aims to increase the solubility of the glass, Aluminium Fluoride (AlF3) metal when added in phosphate glass medium can improve high transparency and thermal stability (Francisco-rodrigueza et al., 2018). Because fluoride has the advantage of improving photoluminescence properties due to low phonon energy. The rare earth ion used in this research is terbium ion (Tb^{3+}).

RESEARCH METHOD

This research was conducted at the Centre of Exellence in Glass Technology and Material Science (CEGM), Faculty of Science And Technology NPRU Thailand. in March - May 2023. The materials used were phosphate, lithium oxide, aluminium flouride, sodium oxide, potassium flouride, terbium. The method used to synthesise Tb^{3+} ions with phosphate glass and a variety of Flouride compounds was melting-quenching. The melt-quenching technique is the process of melting chemicals that are homogeneously mixed at a certain temperature

RESULT AND DISCUSSION

Result

Tb3+-doped glasses have been of interest to many researchers, due to their potential as a laser host matrix. In this study, we used a mixture of fluoride materials to increase the quantum efficiency and high potential power of the glass. The composition of the glass mixture used: $20Li_2O–10AlF_3–69P_2O_5–1Nd_2O_3$ (LAPTb), $20Li_2O$-$10AlF_3$-$10NaF$-$59P_2O_5$-$1Nd_2O_3$ (LANPTb), $20Li_2O$ -$10AlF_3$-$10NaF$-$10KF$-$49P_2O_5$-$1Nd_2O_3$ (LANKPTb). In glassmaking, the material is melted at 1100^{0}C and held for 2 hours.

After that, the melt-quenching method is used with a drastic temperature drop to furnace 350^{o}C to eliminate thermal stress in the glass. Figure 1 represents the glass that has been cut and polished to size for testing the physical properties, structure and optical properties of the glass.

Infrared spectroscopic analysis was used to obtain complete information regarding the compositional makeup of the glass. The inertness and compactness of the samples was demonstrated by the fact that the position and number of FTIR bands did not change, while adding NaF had a minor effect on the intensity, adding KF to the glass samples had a significant effect (Sarumaha et al., 2011).

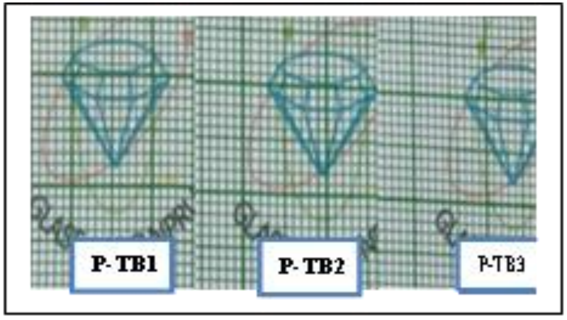

Figure 1. Cut and smoothed glass material doped with Tb^{3+} ions

Table 1. physical properties of glass materials

Physical Properties	Glass Sample		
	P-TB1	P-TB2	P-TB3
Molarity, $M(g)$	115,97289	105,97729	97,59262
Density, $\rho(\frac{g}{cm^3})$	2,5572	2,6675	2,5367
Molar Volume, $V_m(\frac{cm^3}{mol})$	45,3532	41,4394	38,4737
Refractive Index, n	1,5226	1.5227	-
Ion Concentration, $N(\times \frac{10^{22} ion}{cm^3})$	1,33	1,44	1,56
Polaron Radius, $\boldsymbol{r}_p(\text{Å}) \times 10^{-8}$	7,8998	7,6856	7,47733
Distance Core, $\boldsymbol{r}_i(\text{Å}) \times 10^{-8}$	1,9603	1,9074	1,8557
Dielectric Constant, ε	2,3183	2,3186	-
Molar Recrativity, $R_m(cm^{-3})$	13,8456	12,6528	-
Oxide ion polarisability, $\alpha_m(\times 10^{-20} cm^3)$	2,4913	2,0973	-
Metallisation criteria, M	0,6947	0,6946	-
Reflection Loss, $R(\%)$	4,2918	4,2931	-

The % intensity was also found to increase when fluoride compounds (NaF and KF) were added to the sample, it was seen that oxygen bonds decreased by adding more fluoride (Sarumaha et al., 2023). In the research conducted by Hutahaean et al (2022) also explained that the addition of fluoride to the glass can support high pandaran intensity. The relationship between infrared absorption peaks and cluster functions observed with FTIR has been summarised in table 2.

Table 2. Peak position of FTIR spectrum on Phosphate glass

Absorption Area (cm^{-1})	Description
765	Symmetry stretching vibrations that bridge the oxygen of the P-O-P bonds
900	The existence of asymmetric strains in the P-O-P bonds
1263	Asymmetry strain mode (P- O)-
1665	The presence of H-O- H and P-OH bending vibrations in the tissue.

In this observation, it is assumed that the vibrations of the group of atoms in the glass network do not affect the surrounding group in the glass. The vibrational spectra for Tb:Phosphate glasses recorded from the 700-4000 cm^{-1} range can be seen in Figure 2. However, the band at 765 cm^{-1} indicates symmetrical stretching of the oxygen bridging the P-O-P. Whereas 900 cm-1 and 1089 cm-1 and 1146 cm-1 are P-O-P and P=O asymmetric stretches. This band is also a strong band with increased intensity when adding sodium fluoride to the glass. This band shows more structural changes in Tb2 glass. This shows that Tb2 and Tb3 glass have higher frequencies than Tb1 glass. Asymmetric stretching mode (P-O) was assigned at 1263 cm-1. Another weak band at 1665 cm-1 was assigned to bending vibration of H-O-H and P-OH in the network. The addition of fluoride samples will make the intensity decrease in the range of 2000-4000 cm-1 is the hydroxyclic O-H and OH groups in the tissue (Hutahaean et al., 2023).

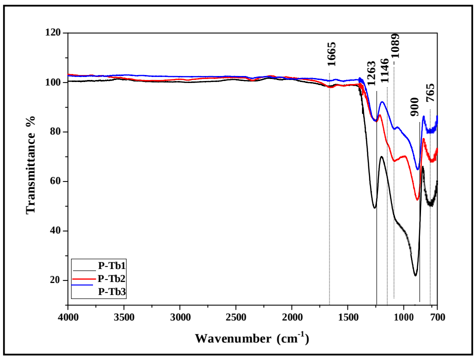

Figure 2. FTIR spectra on glass Tb:Phosphate

Absorption Spectrum

The Tb:phosphate glass system observed in this study consists of three samples labelled P-Tb1, P-Tb2, P-Tb3 respectively. The absorption band cross-section spectra and absorption peaks for the three samples are shown in Figure 3.

The position information and absorption band transitions in Figure 3 are useful for determining the wavelength of light that will be used to excite electrons in the glass medium. This absorption spectrum also plays a role in determining the multiplicity of harmonic generation of light when applied in a laser pumping system.

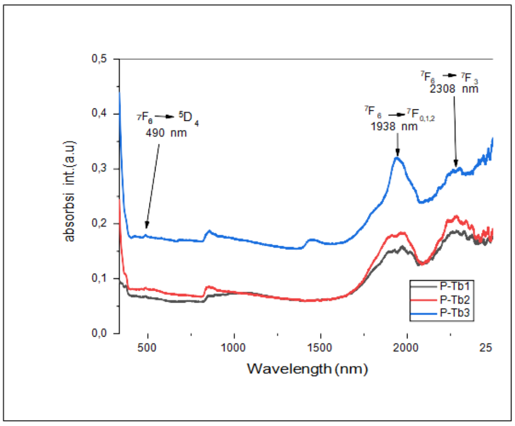

Figure 3. Absorption spectrum on Tb glass: Phosphates

Figure 3 above shown the absorption spectrum of glass phosphate media recorded in the range of 400-2500 nm. The figure shows three absorption bands at 490 nm, 1938nm, 2308 nm. In the UV-VIS region, the weak absorption band observed at a wavelength of 490 nm is assigned to the transition of Tb3+ from the ground state F6 to the excited state 5D4 for the NIR region two clear absorption bands at wavelengths of 1938 nm and 2308 nm and each corresponds to the transition from the 7F3 state. In addition, the absorbance of these three absorption bands increases with increasing Tb2O3 concentration. The Tb3+ doped glasses show intra-configuration transitions originating from the ground state 7F6 to 5D4, 7F0,1,2, 7F3 which are with 490 nm, 1938 nm, 2308 nm respectively.

Photoluminescence

Luminescence is the most common way of emitting or unrestricted outflow of light from a substance or material. Photoluminescence is a type of luminescence in which a material spontaneously emits light when subjected to optical excitation. This allows the excitation and emission spectra of all three samples to represent luminescence properties. Figure 4 and Figure 5 show that the addition of fluoride to the glass decreased the luminescence spectrum. This suggests that some literature stating that fluoride can increase the luminescence spectrum does not apply to this sample. The excitation spectrum of the Tb sample in Figure 4.5 has been recorded with an emission wavelength of 544 nm, which is the green emission of Tb^{3+} ions.

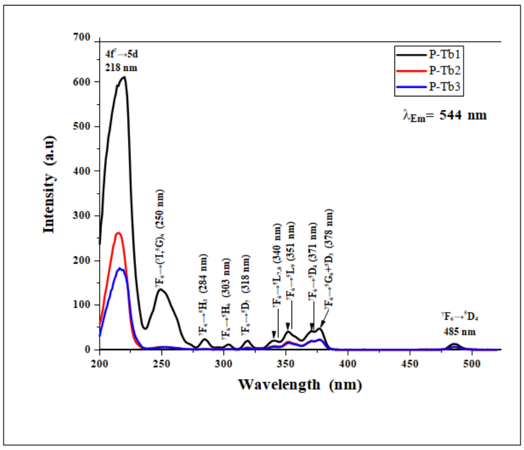

Figure 4. Excitation spectrum of phosphate glass with an observation wavelength of 544 nm

The excitation spectrum in Figure 4. shows the Tb^{3+} doped phosphate glass is in the region of 200-550 nm below the emission wavelength of 544 nm. There are 10 excitation bands shown in Fig. 4. 5 which are at 218 nm, 250 nm, 284 nm, 303 nm, 318 nm, 340 nm, 351 nm, 371 nm, 378 nm, 485 nm transition with $4f^7 \rightarrow 5d$, $^7F_6 \rightarrow (^3I,{}^5G)_6$, $^7F_6 \rightarrow {}^5H_3$,$^7F_6 \rightarrow {}^5H_6$, $^7F_6 \rightarrow {}^5D_7$, $^7F_6 \rightarrow {}^5L_{7,8}$, $^7F_6 \rightarrow {}^5L_9$, $^7F_6 \rightarrow {}^5D_4$, $^7F_6 \rightarrow {}^5G_6 + {}^5D_3$, $^7F_6 \rightarrow {}^5D_4$, $^7F_6 \rightarrow {}^5H_3$ The excitation wavelength was observed at 218 nm and was also clearly visible and selected to excite the glass for emission spectrum measurement.

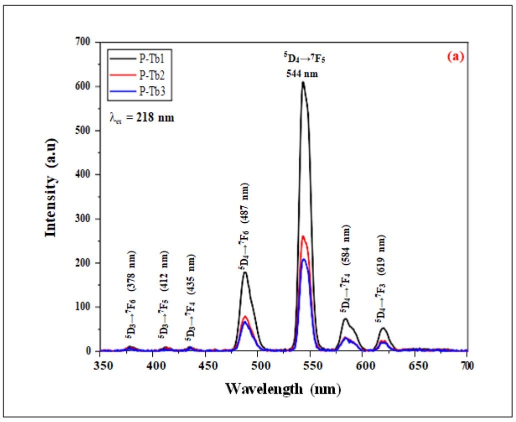

Figure 5a. Emission spectrum of Tb doped with phosphate glass with an excitation wavelength of 218 nm

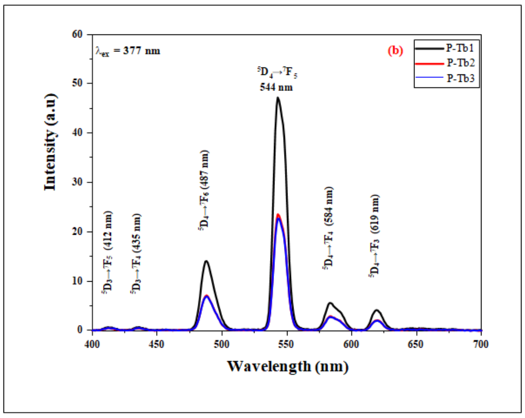

Figure 5b. Emission spectrum of Tb doped with phosphate glass with an excitation wavelength of 378 nm

The emission spectrum of Tb:Phosphate glass in Figure 5 excitation wavelength spectrum is in the region of 350-700 nm below the excitation wavelength of 218 nm. and also shows 7 emission bands at 378 nm, 412 nm, 435 nm, 487 nm, 544 nm, 584 nm, 619 nm. In accordance with the Tb^{3+} emission transition this material produces seven emission band transitions namely 5D3→7F6, 5D3→7F5, $^5D_3 \rightarrow {}^7F_6$, $^5D_3 \rightarrow {}^7F_5$, $^5D_3 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ which is produced from each glass. In this study, the emission peak positions of the seven transitions were at wavelengths of 378 nm, 412 nm, 435 nm, 487 nm, 543 nm, 584 nm, 629 nm, respectively. Tb:Phosphate consistently produced the following emission bands when excited by light at 218 nm, the phosphate glass media showed the same pattern and position. The intensity of each excitation spectrum has a significant impact on the band intensity of the glass medium. The higher the excitation force of the glass medium, the higher the emission power created by the medium (Marbun A., 2018).

CIE (Commission International De I'eclairage) Chromaticity diagram This Commission International de I'Eclairage (CIE) chromaticity diagram is commonly used to analyse the emission colour, which describes the chromaticity visible to the human eye (Wantana et al., 2019), and to evaluate the emission colour (Kaewnum et al., 2018). This CIE chromaticity diagram is calculated to determine the visible luminescence properties of the emission spectral features. The stimulation level required to match the colour of a given power spectral density P(λ) is evaluated using the three equations 1 to 3.

$$X = \int \bar{x}(\lambda)P(\lambda)d\lambda \tag{1}$$

$$Y = \int \bar{y}(\lambda)P(\lambda)d\lambda \tag{2}$$

$$Z = \int \bar{z}(\lambda)P(\lambda)d\lambda \tag{3}$$

Where, $\bar{x}, \bar{y}, \bar{z}$ are CIE diagram matching functions; while X, Y and Z are tristimulus values that provide RGB (red, green, blue) colour stimulation values to match the colour P(λ). Then, the CIE chromaticity coordinates can be calculated using the X, Y and Z values with Equation 4.5 to Equation 4, 5.

$$x = \frac{X}{X+Y+Z} \tag{4}$$

$$y = \frac{Y}{X+Y+Z} \qquad (5)$$

The glass samples were counted and fell in the green region, as shown in Figure 4.7. Since the mole % of Tb3+ ions is adjusted at one mole %, there is no significant difference between the x and y values of the CIE diagram. The coordinates obtained were (0.412142; 0.458453), (0.332228; 0.484787), and (0.328163; 0.5011996) for P-Tb1, P-Tb2, and P-Tb3 glasses, respectively. The coordinates show that all Phosphate glass samples doped with Tb_2O_3 emit a coordination of radiant emissions that are close to each other so that all coordinates can be approximated by an average of (0.35; 0.47). The CIE chromaticity diagram for phosphate glass shown in Figure 6 concludes that the emission of glass samples is shown in the green region (Rajagukguk et al, 2021).

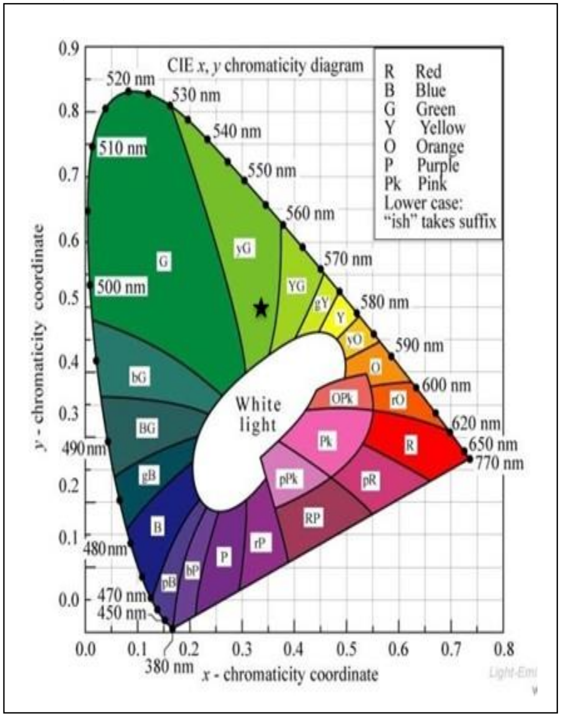

Figure 6. CIE diagram of Tb^{3+} doped Phosphate glass

CONCLUSION AND DISCUSSION

The development of optical material glass medium based on glass materials is a popular topic and continues to be researched, especially in the field of optics and lasers. In this study, it is reported the manufacture of glass medium doped by Tb3+ ions to be applied as a green laser or green lighting.

Based on a series of studies that have been carried out and a number of discussions described in the following chapters, it is concluded that:

1. Based on the measurements and calculations conducted, the physical properties of Tb^{3+}-doped glass materials were obtained. These include molar weight, molar volume, polaron radius, and inter-nuclear distance, all of which decreased in the P-Tb2 and P-Tb3 samples. The refractive index in these two samples increased slightly; however, for the P-Tb3 sample, the refractive index could not be characterized. As a result, other physical properties such as dielectric constant, molar refractivity, polarizability, metallization criteria, and refraction loss could not be determined for this sample, as they are dependent on the refractive index. The density of P-Tb1 and P-Tb2 glass samples showed a slight increase, while the P-Tb3 sample experienced a sharp decline. This is attributed to the P-Tb3 sample being highly hygroscopic and unstable in ambient conditions. Furthermore, the molar volume decreased with the addition of fluoride compounds to the glass. Adding sodium and potassium fluoride to the Tb^{3+}-doped glass resulted in a reduction in the molecular weight of Tb^{3+}.
2. The addition of fluoride compounds, both sodium and potassium fluoride, to the phosphate glass medium doped with Tb^{3+} ions resulted in a decrease in photoluminescence intensity in both the excitation and emission spectra. This is due to the high transmission in the emission region, which can reduce the luminescent ability of the glass sample. The glass sample exhibits strong absorption capabilities due to the interaction between the emitted

light and the structure and composition of the glass.

3. The addition of fluoride compounds, both sodium and potassium fluoride, significantly affects the optical properties of the glass medium, where the incorporation of fluoride increases the absorption intensity.

REFERENCE

Altaf, M & Chaudry, M.A. (2010). Physical Properties Of Litihium Containing Cadium Phosphate Glass. Journal Of Modern Physics. 1(4):201-205.

Djamal, M., Rajagukguk, J., Hidayat, R., Suprijadi, & Kaewkhao, J. (2016). Enhanced 1057 Nm Luminescence Peak and Radiative Properties of Laser Pump Nd3+-Doped Sodium Borate Glasses. Proceedings - 2015 4th International Conference On Instrumentation, Communications, Information Technology And Biomedical Engineering, ICICI-BME2015, 248–253.

Francisco-Rodrigueza, H. I., Lirab, A. A., Meza-Rochad, A. N., Bordignone, S., &Caldiñoc, U. (2018). Bahan Optik GelasFosfat Lithium-Aluminium-SengDiaktifkan Dengan Tb3 + Dan Tb3 + / Eu3 + Untuk Aplikasi Medium Laser Hijau, Oranye Kemerahan Dan Fosfor Putih. Optical materials.79(4):358–365.

Hutahaean, J., Rajagukguk, J., & Simanullang, E. (2023). The Effect of Alkali-Fluoride on the Photoluminescence Properties of Tb3 + Doped on Phosphate Glass Medium. 1080, 155–164.

Hutahaean, J., Rajagukguk, J., Rajagukguk, D., Sarumaha, C., Wantana, N., & Kaewkhao, J. (2022). The Effect Of Sodium Fluoride In Lithium Fluorophosphate (LFP) Glasses Doped With Nd2O3 Ion. Integrated Ferroelectrics, 224(1);100–109.

Rajagukguk, J., Hidayat, R., Djamal, M., Ruangtaweep, Y., Horprathum, M., & Kaewkhao, J. (2016). Structural And Optical Properties Of Nd3+ Doped Na2O-Pbo-Zno-Li2O-B2O3 GlassesSystem. In Key Engineering Materials,675(1):424-429.

Rajagukguk, J., Panggabean, J. H., Sarumaha,C., & Rajagukguk, D. H. (2022). Medium Gain Laser Neodymium (Nd3+) Berbasis Sistem Gelas Borat Dan Fosfat. Cattleya Darmaya Fortuna. Aksess

di https://www.google.co.id/books/editio n/Medium_Gain_Laser_Neodymiu m_ Nd3+_Berbasi/Un2feaaaqbaj?hl=id &gb pv=1&dq=gambar+ikatan+silang+fo sfat &pg=PA19&printsec=frontcover.

Rajagukguk, J., Rahmaniar, Harahap, N., Situmorang, R., Panggabean, D. D., & Kaewkhao, J. (2021). Preparation and Structural Characterization of Dy3+- Doped PBiNaGd Glass. Integrated Ferroelectrics, 214(1), 151-157.

Rajagukguk, J., Sarumaha, C. S., Chanthima, N., Wantana, N., Kothan, S., Wongdamnern, N., & Kaewkhao, J. (2021). Radio And Photo Luminescence Of Dy3+ Doped Lithium Fluorophosphate Scintillating Glass. Radiation Physics And Chemistry, 185(April), 109520.

Ramteke, D. D., Balakrishna, A., Kumar, V., & Swart, H. C. (2017). Luminescence Dynamics And Investigation Of Judd- Ofelt Intensity Parameters Of Sm3+ Ion Containing Glasses. Optical Materials, 64, 171–178

Sarumaha, C. S. ., Rajagukguk, J. C.,

Chanthima, N. A., Kidkhunthod, P. D., Chanlek, N. D., Kantuptim, P., Yanagida, T., F, H. J. K., & Kaewkhao, J. A. (2023). Fisika Radiasi dan Kimia Karakteristik pendaran Ce 3 + gelas multikomponen litium fluorofosfat yang diolah. Radiation Physics and Chemistry, 207,10814.