Preparation and Characterization of Nd$^{3+}$ doped P$_2$O$_5$-Bi$_2$O$_3$-Na$_2$O-Gd$_2$O$_3$ Glasses System for Laser Medium Application

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Abstract. Neodymium doped phosphate glass system with composition (70-x)P$_2$O$_5$-10Bi$_2$O$_3$-10Na$_2$O-10Gd$_2$O$_3$-xNd$_2$O$_3$ (x=0; 0.05; 0.1; 0.5; 1.0; 3.0 mol%) have been prepared and characterized. All chemical compounds in powder form with a total mass of 20 grams are mixed in containers porcelain crucible with melt-quenching technique at 1200°C. The physical properties include: density, molar volume, refractive index, polaron radius and susceptibility were investigated by using Archimedes principle and mathematical calculation. From the absorption spectra can be obtained that the absorption band centered at ten transition peaks. The XRD result show that the glass structure be amorphous nature (no sharp peaks). The sample density also increases slowly following the increase in the concentration of Nd$^{3+}$. The refractive index gradually increases from 1.63 for undoped glass to 1.673 for 3.0 Nd$^{3+}$ doped glass.

Keywords: Phosphate Glasses, Laser Medium, Nd$^{3+}$

1.Introduction

The rapid development of science and technology, providing great benefits for human life, especially in the field of optics and telecommunications. At the same time, because optical reinforcement technology is mostly made of glass or sometimes also from other materials, various studies have emerged that show physical symptoms or nonlinear properties of materials for the development of exciting new technologies. Thus, optical amplifier technology needs to be studied not only by its electrical properties but also by its optical properties. Tain rare earth element are very interesting to study because their macroscopic properties such as high mechanical resistance, chemically stable and good heat resistance. Rare earth ions are lanthanide (trivalent lanthanide) active ions in the periodic system of elements. Utilization of glass material as a medium for hosting neodymium ions (Nd$^{3+}$) was first introduced by Snitzer (1961). From the research [1] neodymium is one of the active ions which is not only developed for industrial and research applications, but also the tendency of lasing properties to vary with the composition of Nd$^{3+}$ and [2] adding that exposure to phosphate glass (Nd:Phosphate) promises.
Some promising applications of the use of Nd\textsuperscript{3+} ions in doping in glass material (Nd: glass) from research [3] include optical amplifiers, wave guides, optical fibers and optical data storage systems. In addition to playing an important role in optical communication, Nd: glass phosphate is also very promising especially in the infrared (IR) wavelength range. This is reinforced by the results of a study by [2] Nd\textsuperscript{3+} ions exposed to phosphate glass, showed that there was luminescent emission at the level of \textsuperscript{4}F\textsubscript{3/2} to \textsuperscript{4}I\textsubscript{9/2}.

According from research [4] it has interesting and distinctive properties such as high expansion coefficient, low melting temperature, and good optical and UV-Vis transmission characteristics. Phosphate glass (P\textsubscript{2}O\textsubscript{5}) is the ideal material for many applications including laser host, low frequency solid waves, photoconductors, biomaterials, glass-polymer composites, laser sources of solids, amorphous semiconductors and optical fibers. And also [5] added that phosphate glass is an attractive host because it can accommodate active ions without losing their characteristic properties and has a high thermal expansion coefficient, high refractive index, low dispersion, low melting point, electrical conductivity the high and varying structures to receive some exchange of cations and anions.

Prepared glass material according [6] based on the nature of ionic bonding on glass cation bonds, there are three main constituent components, namely formers, intermediates, and modifiers. Given the poor chemical resistance to glass phosphate as a former, the presence of modifiers or other glass material formers can improve the value of the chemical resistance of the glass so that it forms a glass material that can be applied as an optical amplifier. In the study of [7] showed that the addition of various oxides, especially high valence metal oxides such as SnO, PbO, ZnO, Cr\textsubscript{2}O\textsubscript{3}, Gd\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}O produce structural changes in structure that can be associated with the structure of phosphate tissue. According to [8] Na\textsubscript{2}O as a modifier aims to increase solubility, while Bi\textsubscript{2}O\textsubscript{3} as a stabilizer aims to increase the viscosity of glass material and has good transparency in the visible and near infrared [9].

Various studies to obtain a optical amplifier in the fixed medium cannot be separated from the influence of the physical properties and optical properties of the glass used as the optical strengthening medium. In the research of [10] has been successful in making glass material with melt-quenching technique where X-ray diffraction patterns indicate that the glass is amorphous. From the results obtained also showed that the density and energy gap values decreased while the molar volume, energy Urbach and refractive index increased with a high refractive index value of 2.63.

Another study by [9] using tellurite glass was successfully fabricated with the results obtained by adding PbO elements which have high polarizability ion values resulting in good density, refractive index, and an increase in optical band gap energy. And also [8] added from the results of his study that glass based tellurite doping Nd\textsuperscript{3+} had a high refractive index increasing from 1.825 to 2.081 with increasing concentration of Nd\textsuperscript{3+}O\textsubscript{3} from 0.5 mol to 2.5 mol\% [11] used glass Nd: Phosphate with the results obtained by the glass refractive index gradually increasing 1.523 undoped to 1.534 Nd\textsuperscript{3+} 2.0 mol\%. As well as fabricated glasses have a good level of hardness and high transparency as the addition of Nd\textsuperscript{3+} ion concentration into the glass composition.

Thus, although it has been developed in several further study studies to obtain phosphate glasses exposed to Nd\textsuperscript{3+} ions with optimum results, it is still very necessary. Based on this description, researchers are interested in examining the effect of variations in the concentration of active ion Nd\textsuperscript{3+} on optical properties as an optical reinforcement material. Where physical properties are obtained by calculating Archimedes' principles and optical properties with characterization using Abbe Refractometer, XRD, FTIR, UV-Vis NIR, and Spectrofluorophotometer.
2. Experimental

2.1. Materials

The main glass preparing element used in this research is phosphorus pentoxide (NH$_4$H$_2$PO$_4$) which is doped using Neodymium active ion (Nd$_2$O$_3$) using melt-quenching technique. The composition of the glass and active ion systems used in this study is written in the form of chemical formula: \((70-x)\) P$_2$O$_5$-10Bi$_2$O$_3$-10Na$_2$O-10Gd$_2$O$_3$-xNd$_2$O$_3$ mol% with \((x = 0.0; 0.05; 0.1; 0.5; 1.0; 3.0)\). Where \(x\) is the percentage of molecular weight of Nd$^{3+}$ ion doped in a glass system. All materials used are powder and have a purity of 99.9%.

2.2. Instrumentation

Structural analysis was performed using X-ray diffractometer (XRD Shimadzu) with the light source the glass structure be amorphous nature. Infrared absorption analysis was performed using Fourier Transform Infrared (FT-IR) Alpha Platinum ATR A220 / D-01 with range wave number of 500-4000 cm$^{-1}$. Abbe Refractometer analysis was Physical properties of glass. To analyze the absorption spectrum of glass material using Uv-Vis NIR and emission spectrum using instrument Spektrofluorophotometer.

2.3. Melt-quenching technique

Melt-quenching technique is the process of melting chemicals that have been mixed homogeneously at a certain temperature.

3. Results and Discussion

3.1 Glass Display

Initial fabrication results on the physical shape of the glass Nd: Phosphate before cut and polish shown in Figure 3.1 obtained glass with a high level of transparency, homogeneous, and not cracked. The size of the mass of each glass phosphate system constituent can be seen in Table 3.1 where the mass of the glass medium modifier decreases with the addition of Nd$^{3+}$ ions. Samples with Nd$^{3+}$ ion concentration of 3.0 mol% appear to have a darker color than other materials due to the number of Nd$^{3+}$ ions which occupy the glass host more closely.

| Symbol/ comp. | PBN | PBN1 | PBN2 | PBN3 | PBN4 | PBN5 |
|---------------|-----|------|------|------|------|------|
| P$_2$O$_5$    | 10.5475 | 10.5346 | 10.5216 | 10.4435 | 10.3482 | 9.9933 |
| Gd$_2$O$_3$  | 3.8480 | 3.8461 | 3.8441 | 3.8183 | 3.7861 | 3.6589 |
| Na$_2$O      | 0.6579 | 0.6575 | 0.6572 | 0.6528 | 0.6473 | 0.6255 |
| Bi$_2$O$_3$  | 4.9463 | 4.9438 | 4.9412 | 4.9080 | 4.8667 | 4.7032 |
| Nd$_2$O$_3$  | 0.0000 | 0.0178 | 0.0356 | 0.1772 | 0.3514 | 1.0188 |
| **Total**    | **20 gr** | **20 gr** | **20 gr** | **20 gr** | **20 gr** | **20 gr** |
To obtain a finer and more transparent glass, it is necessary to cut and polish as shown in Figure 3.2.

![Fig. 3.2](image2)

**Fig. 3.2** Glass samples after cut and polish with value (pxlxt = 1.0mm* x 0.2mm* x 1.5mm* ) doped Nd**3+** and concentration respective samples.

### 3.2 Physical Properties of Glass

As for the physical properties of the glass medium Nd: Phosphate as well as the refractive index (n), density (ρ), the concentration of Nd**3+** ions and these parameters can be obtained using the Archimedes Method physics. Results of concern for physical properties for glass Nd: Phosphate is shown in Table 3.2. The density of the glass is usually considered to be an essential characteristic for controlling the quality of the glass. Changes in observations of glass density are directly affected by differences in glass composition and ultimately affect tissue structure.

**Table 3.2 Physical properties of doped Nd**3+** with composition (70-x)P2O5-10Bi2O3-10Na2O-10Gd2O3-xNd2O3**

| Measurement            | Undoped | PBNGNd1 | PBNGNd2 | PBNGNd3 | PBNGNd4 | PBNGNd5 |
|------------------------|---------|---------|---------|---------|---------|---------|
| Massa molar (g/mol)    | 188.405 | 188.502 | 188.599 | 189.377 | 190.350 | 194.241 |
| Kerapatan (g/cm³)      | 3.563   | 3.547   | 3.560   | 3.561   | 3.597   | 3.697   |
| Volume molar (cm³/mol) | 52.882  | 53.143  | 52.976  | 53.180  | 52.909  | 52.531  |
| Konsentrasi ion Nd**3+** (Nx10²²/cm³) | 0.000   | 0.06    | 0.11    | 0.57    | 1.14    | 3.44    |
| Polaron radius (Å)     | 0.000   | 0.16    | 0.20    | 0.33    | 0.421   | 0.608   |
The results of the calculation of variations in Nd\(^{3+}\) ion concentration to density (\(\rho\)) and molar volume (VM) are shown in Table 3.2. Where the refractive index (\(n\)), density (\(\rho\)), field strength (\(F\)), dielectric constant (\(\varepsilon\)), molar refractivity (\(R_m\)), susceptibility, and polarization of oxide ions (\(\alpha_{m}\)) increase in value along with increasing Nd\(^{3+}\) concentration in the glass. In contrast to the molar volume (VM), the polar radius and the inter nuclear distance decrease with increasing Nd\(^{3+}\) concentration in the phosphate glass. Decreasing the molar volume in the glass indicates that the glass structure is getting denser with the addition of Nd\(^{3+}\) ion concentration.

The relationship of variations in Nd\(^{3+}\) ion concentration to density (\(\rho\)) and molar volume (VM) is shown in Figure 3.3. From the graph, the result shows that the glass density increases with increasing Nd\(^{3+}\) ion concentration from 0.05 to 3.0 mol%.

![Graph density and molar volume of glass doped Nd\(^{3+}\)](image-url)
3.3 Structure of Nd: Glass

Glass X-ray diffraction pattern Nd:Phosphate is shown in Figure 3.4 where the spectrum pattern shows the same shape ie no sharp peaks are found along the diffraction angle (2θ) observation area, but there is a wide form of mound around the diffraction angle 28°. This indicates that there is no crystal characteristic in the glass material so that it can be expressed as glass Nd:Phosphate is amorphous (no sharp peaks).

![Fig. 3.4 X-ray diffraction pattern of glass (70-x)P2O5-10Bi2O3-10Na2O-10Gd2O3 xNd2O3(x=3.0%mol PBNGNd6) doped of Nd3+](image)

Infrared spectroscopy analysis is used to obtain complete information regarding the composition of the glass composition. The relationship between the infrared absorption peaks of the corresponding cluster functions observed with the Fourier Transform Infrared (FTIR) has been summarized in Table 3.3.

| Absorption area (cm⁻¹) | Clarification |
|------------------------|---------------|
| 720-770                | Symmetric strain vibrations of tying P-O-P to be expressed (POP)_s |
| 871                    | There is an symmetric strain of tying P-O-P (POP) |
| 1019                   | Modus symmetric strain of effect non-bridging oxygen of group O-P-O |
| 1231                   | Asymmetric strain vibrations between P-O in group (PO₂) to be (PO₂)as |

In this observation it is assumed that the vibration of groups of atoms in the glass tissue does not affect the other surrounding groups in the glass. Vibration spectrum for glass Nd:Phosphate recorded from an area of 600 cm⁻¹ to 1400 cm⁻¹ can be seen in Figure 3.5. There is a position of absorption band that appears on the glass structure Nd:Phosphate which is between 720 cm⁻¹ to 770 cm⁻¹, 871 cm⁻¹, 1019 cm⁻¹, and 1231 cm⁻¹. Absorption bands that occur in the 720-770 cm⁻¹ region are caused by symmetric strain vibrations in the P-O-P bond which can be expressed as (POP)s.
The presence of absorption bands at wave number 871 cm$^{-1}$ is characterized by the presence of asymmetric strain on P-O-P (POP) bonds. This absorption band indicates that phosphate tissue is constructed from short chains and pyrophosphate group (P2O$^7_{4-}$) because of its position between the sodium phosphate chain (NaPO$_3$) in the area of 816 cm$^{-1}$ with sodium pyrophosphate (942 cm$^{-1}$) (Tiwari, 2007). Next is the absorption band around 1019 cm$^{-1}$, which occurs for all glass medium Nd:Phosphate. This states the symmetrical strain mode through the non-bridging oxygen effect of the O-P-O group, which indicates the formation of $Q^2$ tetrahedral phosphate formation (Jha et al, 2015). Finally, the absorption band at 1231 cm$^{-1}$ shows the asymmetric strain vibration process between P-O in the group (PO$_2$) which can be referred to as (PO$_2$) as (Meyer, 1997) and this absorption band decreases with reduced phosphate composition in the glass.

### 3.4 Optical Absorption Properties Glass Nd: Phosphate

Glass system Nd: Phosphate observed in this study consisted of 5 types of samples with each label PBNGNd1 (0.05Nd$^{3+}$), PBNGNd2 (0.1Nd$^{3+}$), PBNGNd3 (0.5Nd$^{3+}$), PBNGNd4 (1.0Nd$^{3+}$), and PBNGNd5 (3.0Nd$^{3+}$). The spectrum of absorption bands for the five glass mediums is shown in Figure 3.6. Seven absorption peaks can be produced by PBNGNd glass medium, eight absorption peaks can be produced by PBNGNd2 glass medium while PBNGNd3, PBNGNd4, and PBNGNd5 glasses show eleven absorption bands obtained. The absorption band in the glass appears at the beginning of the wavelength of 362 nm which follows the transition pattern $^4I_{9/2} \rightarrow ^4D_{7/2} + ^2I_{15/2}$. The transition and absorption band position along with the energy level for all glasses Nd: Phosphate is shown in Table 3.5.
Fig. 3.6. Absorption spectra of 0.05 to 3.0 mol% of Nd$_2$O$_3$ doped phosphate glass.

It appears from Figure 4.6 that the glass sample Nd: This phosphate can produce light emission if with several choices of laser wavelengths such as 526 nm, 582 nm and 805 nm. The laser used to excite in this study is a 582 nm laser. Of all absorption transitions produced by glass Nd: Phosphate there is one of the most sensitive peaks, so-called hypersensitive transitions namely $^4I_{9/2} \rightarrow ^2G_{7/2} + ^4G_{5/2}$ transitions at a wavelength of 522 nm. The hypersensitivity transition occurs in the same position for all glasses Nd: Phosphate.

Table 3.4 Absorption band position and level energy of glass Nd:Phosphate

| Transition | PBNGNd1 | PBNGNd2 | PBNGNd3 | PBNGNd4 | PBNGNd5 |
|------------|---------|---------|---------|---------|---------|
| $^4I_{9/2} \rightarrow ^4I_{13/2}$ | 362 | 27.624,31 | 362 | 27.624,31 | 362 | 27.624,31 |
| $^2D_{3/2}$ | 379 | 26.385,22 | 379 | 26.385,22 | 379 | 26.385,22 |
| $^2P_{1/2}$ | - | - | - | - | 407 | 24.570,02 |
| $^4G_{11/2}$ | 451 | 22.172,95 | 451 | 22.172,95 | 451 | 22.172,95 |
| $^2G_{9/2}$ | 488 | 20.491,80 | 488 | 20.491,80 | 488 | 20.491,80 |
| $^2G_{7/2}$ | 522 | 19.157,09 | 522 | 19.157,09 | 522 | 19.157,09 |
| $^4G_{7/2}$ | 544 | 18.382,35 | 544 | 18.382,35 | 544 | 18.382,35 |
| $^4H_{11/2}$ | 652 | 15.337,42 | 652 | 15.337,42 | 652 | 15.337,42 |
| $^4F_{5/2}$ | 802 | 12.468,83 | 802 | 12.468,83 | 802 | 12.468,83 |
| $^4I_{0/2}$ | 859 | 10.224,95 | 859 | 10.224,95 | 859 | 10.224,95 |

It appears in table 3.4 that most of the same transition for each glass is in the same position (wavelength). But this does not apply to all samples meaning that not the same transition is always at...
the same wavelength. The difference in the position of this wavelength arises as a result of partial expansion of the skin caused by the shift of the charge from the ligand to the nucleus of the ion center. This condition is often expressed as a nephelauxetic effect which can directly affect the molar volume of the glass medium.

4. Conclusions

Phosphat glasses doped with (0.05, 0.1, 0.5, 1.0 and 3.0 mol%)Nd$_2$O$_3$ were prepared and characterized. The XRD result shows that the glass structure be amorphous nature. The sample density also increases slowly following the increase in concentration Nd$^{3+}$ from 1.63 for undoped glass to 3.0 Nd$^{3+}$ doped glass.

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