Physical, Structural, and Raman Spectroscopic Traits of Neodymium-Doped Lead Oxyfluoride Zinc Phosphate Glass

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Abstract. Nd³⁺ with composition of (60 - x) P₂O₅ - 10ZnO - 30PbF₂ - (x) Nd₂O₃ where (0.0 ≤ x ≤ 2.0 mol %) was prepared using a melt-quenching approach to the development of transparent glasses. These glasses have been confirmed to be an amorphous structure through XRD analysis. The glass density, molar volume and ionic packing density were obtained in the range of 3.978-4.157 g cm⁻³, 41.949 - 41.073 cm³ mol⁻¹ and 0.614-0.624, respectively. Using Fourier Transform Infrared (FTIR) and Raman Spectroscopy, the chemical functional groups and biomolecules of samples were characterised. The FTIR spectra revealed six main bands assigned to P-O, P-O-P, P=O, (PO₃)²⁻ and hydroxyl groups (O-H), while Raman shift detected five symmetric and asymmetric bands attributed to P-O-P bonds in Q₁ units, (PO₃)³⁻ bonds in Q₀ units, (PO₃)²⁻ bonds in Q₁ units, (PO₃)¹⁻ bonds in Q² units and P=O bonds in Q³ units. It is believed that the proposed oxyfluoride glasses may be useful and suitable applicant to lasing materials and sensors sensitivity.

1. Introduction

Oxyfluoride zinc phosphate glass provides a broadly range alternative of applications for optical components such as laser windows and fiber optic communications especially for IR-transmitting materials. Obtaining more than one glass modifiers like ZnO and PbF₂ play a huge structural role that is
concerned to follow the properties alteration with changing in composition series of \( \text{P}_2\text{O}_5 - \text{ZnO} - \text{PbF}_2 - \text{Nd}_2\text{O}_3 \) glass system [1]. Phosphate glasses have been developed and manufactured for numerous potential applications in technologies such as amplifiers, optical fibers, solid state lasers sensing, energy storage devices, high ultraviolet, long wavelength infrared transmissions and telecommunication fibers [1]. However, it limited in exploiting both electrical conductivity and dielectric properties are still under exploring due to incorporation of \( \text{Nd}_2\text{O}_3 \) concentration on the structure in the composition of lead oxyfluoride zinc phosphate glass systems [2]. Behavioural characteristic of \( \text{Nd}^{3+} \) ions on structural properties has not been fully understood [3, 4].

Several reports were done on \( \text{Nd}^{3+} \) ions to build up the spectroscopic, optical and thermal properties of phosphate-based glass systems [5, 6, 7]. However, there is still lack of findings which requires more understanding on the physical and structural of \( \text{Nd}_2\text{O}_3 \) doped phosphate-based glass in order to obtain the density, molar volume, ionic packing density, structural bonding, AC conductivities and impedance characteristics. It is very important to know that the varying of concentration of the \( \text{Nd}^{3+} \) ions on host glasses have significant effects on its physical properties for suitable usages.

In terms of industrial applications purpose [7], it is required to assess the effect of different concentration of \( \text{Nd}^{3+} \) doped to a series of glass compositions on physical and structural properties. A thoroughly preparation and characterisation of the glass samples is needed for a better understanding of the properties of these prepared glass samples in the presence of various concentrations of RE ions in phosphate glass systems. The present work deals with the role of Nd on the structure and physical characteristics of host oxyfluoride zinc-phosphate glass.

2. Experimental

1.1. Preparation of glasses

All chemical reagents (\( \text{P}_2\text{O}_5, \text{ZnO}, \text{PbF}_2 \) and \( \text{Nd}_2\text{O}_3 \)) were used to fabricate the glasses with compositions of \((60 - x) \text{P}_2\text{O}_5 - 10\text{ZnO} - 30\text{PbF}_2 - x \text{Nd}_2\text{O}_3\) by melt quenching technique. The composition and glass labels with different annealing time are summarized in Table 1. The powder was well-mixed and pre-heated for 30 minutes at 350 °C before melted at 1100 °C and annealed at 350°C for 3 hr.

| Samples | Composition (mol%) |
|---------|--------------------|
| S1      | 60.0 10.0 30.0 0.0 |
| S2      | 59.5 10.0 30.0 0.5 |
| S3      | 59.0 10.0 30.0 1.0 |
| S4      | 58.5 10.0 30.0 1.5 |
| S5      | 58.0 10.0 30.0 2.0 |

1.2. Characterization of glasses

X–ray diffraction (XRD) (Siemens Diffractometer D50000) analysis was performed using Cu Kα with a radiation source of wavelength \( \lambda=1.54056 \) Å at 40 kV and 100 mA. Diffraction patterns were collected in the 2θ range from 15° to 75° to identify the amorphousity of the glass samples. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy was implemented on a PerkinElmer FrontierTM Spectrometer and (Unidron Automated Microscope Raman Mapping System) to detect diverse chemical functional groups and biomolecules. Archimedes principle is used to measure the density of the glass by using Prescisa Balance XT 220A. Distilled water is used as the immersion liquid. The density measurement of the glass as given by the equation below,

\[
\rho = \frac{w_a}{w_a - w_i}\left(\rho_l - \rho_a\right) + \rho_a
\]
where $W_a$ refers to the weight of the sample in air whereas, $W_l$ signifies weight in immersion liquid and the density of the immersion fluid (distilled water = 1 g cm$^{-3}$) and density of air (0.001 g cm$^{-3}$) represent by $\rho_l$ and $\rho_a$.

The value of density from above equation is necessary to determine the molar volume $V_m$ by using stated equation as below,

$$V_m = \frac{M}{\rho} \quad (2)$$

where $M$ refers to the molecular weight of the sample calculated to determine the composition of the glass.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 displays the XRD peaks for Sample S5 glass composition of $P_2O_5$ - $ZnO$ - $PbF_2$ - $Nd_2O_3$ with a concentration of 2.0 mol% of $Nd^{3+}$ ions. The XRD measured in the range of $10^\circ \leq 2\theta \leq 100^\circ$ that revealed the presence of broad humps in the region of $25^\circ$ and $40^\circ$ indicates the absence of bubbles and sharp peaks which confirm the non-crystalline and amorphous nature of the prepared glass samples [8].

Figure 1. X-ray Diffraction pattern of Sample S5 of $(60 - x) P_2O_5$ - $10ZnO$ - $30PbF2$ - $(x) Nd2O3$ glass system.

3.2. Physical Properties

The physical properties such as density, molar volume and ionic packing density were obtained for all glass samples. All the measurements values are tabulated in Table 2.

Table 2. Density, $\rho$ molar volume, $V_m$ and ionic packing density $V_t$ of $(60 - x) P_2O_5$ - $10ZnO$ - $30PbF2$ - $(x) Nd2O3$ glass system.

| Samples | Nd$_2$O$_3$ (mol%) | $\rho$ ($\pm0.001$ g cm$^{-3}$) | $V_m$ ($\pm0.001$ cm$^3$mol$^{-1}$) | $V_t$ ($\pm0.001$) |
|---------|-------------------|----------------|-------------------------------|-----------------|
| S1      | 0.0               | 3.978          | 41.949                        | 0.614           |
| S2      | 0.5               | 4.033          | 41.611                        | 0.618           |
| S3      | 1.0               | 4.089          | 41.281                        | 0.622           |
| S4      | 1.5               | 4.129          | 41.116                        | 0.624           |
| S5      | 2.0               | 4.157          | 41.073                        | 0.624           |

Figure 2 shows the variation in density and molar volume of various Nd$_2$O$_3$ concentrations in the $P_2O_5$ - $ZnO$ - $PbF_2$ glass system. To better understanding, the physical characteristics of the synthesized glass system were measured to clarify the structural network of glasses performance. The density and molar
volume are the important parameters which gives information about the glass compactness. The higher density and lower molar volume indicates that the ionic group were tightly packed around each other making the glass structure more compact and closed network of the glass [9]. Where, the glass density was observed to be increased from 3.978 up to 4.157 gcm$^{-3}$ as the concentration of Nd$^{3+}$ is increase. Since Nd$_2$O$_3$ has higher molecular weight (336.477 gmol$^{-1}$) compared to P$_2$O$_5$ (141.943 gmol$^{-1}$) and larger ionic radii that substituted by Nd$_2$O$_3$ in samples with Nd$^{3+}$ ions doping [7]. This reveals the addition of RE ions generates more non-bridging oxygen (NBO) formation, leading the glass structure to undergo modifications [8].

Furthermore, molar volume that is mainly influenced by the density of the glass showed accurately the opposite behaviour to density as predicted. The molar volume observed to decreases from 41.949 up to 41.073 cm$^3$mol$^{-1}$ when the concentration of Nd$^{3+}$ was increased. Indicating that the extra free spaces in the glass network were occupied by Nd$^{3+}$ ions. It was caused by replacement of larger Nd$^{3+}$ with smaller P$^{5+}$ ions, modifying the glass structure network to become more compact [7]. Hence, increasing number of NBO exhibited the reduction of molar volume. In addition, the increase in the concentration of Nd$^{3+}$ ions, the formation of bond linkages between P-O-Nd and other phosphate groups were occurred and tend to give rise to the polymerization reaction in the structure of the glass network. This reaction is responsible for the rigidity as well as the compaction of the glass network that resulted gradual decrease in the molar volume [5].

Figure 3 exemplifies the ionic packing density variation. The trend was found to be increased with the Nd$^{3+}$ ions addition up to 2.0 mol% due to an increase in compactness (enlisted in Table 2). The O$^-$ ions were surrounded by compact electron clouds create more tightly between bonding in glass structure which increased the ionic packing density [10]. Besides, the insertion of higher density of Nd$_2$O$_3$ (336.477 gmol$^{-1}$) than P$_2$O$_5$ (141.943 gmol$^{-1}$) caused increasing in the ionic packing density. Such increase in this value signifies the excess volume which is almost filled by the Nd$^{3+}$ ions [44].

![Figure 2](image2.png)  
**Figure 2.** Density and molar volume at different concentration of Nd$_2$O$_3$.

![Figure 3](image3.png)  
**Figure 3.** Ionic packing density with different concentration of Nd$_2$O$_3$.

### 3.3. FTIR Analysis

Figure 4 demonstrates the FTIR spectra for the glass system recorded in the 400 – 4000 cm$^{-1}$ frequency range. Their frequency and prominent transmission bands were detected on different concentrations of Nd$_2$O$_3$ and enlisted in Table 3. The literature data on the wavenumber ranges serves as a reference source for the identification of the IR bands corresponding to the vibrations of the structural units in various phosphates based glass system. FTIR spectra of the prepared glass sample with different concentration of Nd$_2$O$_3$ revealed six prominent peaks in the spectrum that can be observed in the 400-4000 cm$^{-1}$ wavenumber range. The combination of bonds between Zn-O bending modes and P-O vibrations modes creates a long wavenumber infrared band with a peak around 474 – 482 cm$^{-1}$. Besides, the peak lies
around 777 and 778 cm\(^{-1}\) was due to the symmetrical stretching modes of P-O-P bonds. Asymmetrical stretching of P-O-P bonds was assigned to the absorption band of 898 – 900 cm\(^{-1}\) [11]. In addition, the band occurred around 1053 – 1067 cm\(^{-1}\) corresponding to the (PO\(_3\))\(^2-\) symmetrical stretching mode which was triggered by P\(_2\)O\(_5\) NBO fraction of the tetrahedral particularly with Zn-O content in the network chain structure [11]. The P=O bond induces the asymmetric stretching vibration mode in the glass network at a band around 1251 – 1253 cm\(^{-1}\). Furthermore, the O-H groups created a symmetrical stretching vibration mode in small spectral bands observed at around 3467 – 3480 cm\(^{-1}\), indicating the presence of water content in glass network was due to the ability to absorb water or moisture from powdered phosphate glass during the KBr pellet preparation process [12].

![Figure 4. FTIR spectra of a glass system with various concentration of Nd\(_2\)O\(_3\).](image)

**Table 3. FTIR band assignments of various structural units in the glass system as a function of Nd\(_2\)O\(_3\) concentration.**

| Samples | Nd\(_2\)O\(_3\) mol% | Band Assignment (cm\(^{-1}\)) |
|---------|----------------------|------------------------------|
|         |                      | P-O Bending Vibration | P-O-P Stretching Vibration | P-O-P (PO\(_3\))\(^2-\) Stretching Vibration | P=O Stretching Vibration | O-H Stretching Vibration |
| S1      | 0.0                  | 474             | 778             | 898             | 1053           | 1251           | 3467           |
| S2      | 0.5                  | 474             | 778             | 899             | 1058           | 1253           | 3468           |
| S3      | 1.0                  | 475             | 778             | 900             | 1059           | 1251           | 3480           |
| S4      | 1.5                  | 481             | 778             | 900             | 1064           | 1251           | 3469           |
| S5      | 2.0                  | 482             | 777             | 900             | 1067           | 1251           | 3470           |

3.4. Raman Analysis

Raman spectra for the prepared glass system with an addition of 2.0 mol% of Nd\(^{3+}\) ion in the spectral range of 600 - 1400 cm\(^{-1}\) were shown in Figure 5. The frequency and Raman assignments band extracted were listed in Table 4. As in Figure 5, five prominent peaks were found in the frequency range of 600-1400 cm\(^{-1}\) wavenumber. The P-O-P symmetrical stretching mode of non-bridging bonds in Q\(^1\) units and (PO\(_4\))\(^3-\) symmetrical stretching of non-bridging bonds in Q\(^0\) units occurs near the bands at 731 and 822 cm\(^{-1}\), respectively [13, 14]. The addition of Nd\(_2\)O\(_3\) to the glass system resulted in changes in the P-O-P bond angle where the band shifted to 731 cm\(^{-1}\) wavenumber [15]. The 1092 cm\(^{-1}\) band spectrum is attributed to the (PO\(_3\))\(^2-\) symmetrical stretching mode of non-bridging bonds in Q\(^1\) units. (PO\(_4\))\(^3-\) symmetrical stretching mode of non-bridging bonds is observed near the band at 1191 cm\(^{-1}\) which is known as ‘strained’ where it may contains three- or four-membered rings in Q\(^2\) structural units [16]. P=O symmetrical stretching mode of non-bridging bonds in Q\(^3\) units can be detected near the band at 1352 cm\(^{-1}\). The replacement of P-O-Nd bonds with P=O causes a structural in the main phosphate.
network to rearrange between themselves which affected all the peaks involved [14]. It is clearly showing that the 2.0 mol% of Nd$_2$O$_3$ content was introduced to the glass system, there was a decrease of Q$^1$ chain terminator indicates that the glass network structure becomes more compact and cross-linked. As a consequence, when Q$^1$ terminal oxygen is replaced by P-O-Nd bonds that contributed in the glass network structure, Raman spectra suggested that there is a certain disproportionateness of the Q$^2$ and Q$^0$ units to the Q$^1$ units in the prepared glass samples which may disturbs with the whole arrangement of the glass network structure [14].

![Figure 5. Raman spectrum of glass system with 2.0 mol% concentration of Nd$_2$O$_3$ ranged of 600 - 1400 cm$^{-1}$.](image)

| Raman Shift (cm$^{-1}$) | Assignments | References |
|------------------------|-------------|------------|
| 731                    | P-O-P symmetrical stretching mode of bridging bonds in Q$^1$ units | [16] |
| 822                    | (PO$_4$)$^3_-$ symmetrical stretching mode of non-bridging bonds in Q$^0$ units | [46] |
| 1092                   | (PO$_3$)$^2_-$ symmetrical stretching mode of non-bridging bonds in Q$^1$ units | [47] |
| 1191                   | (PO$_2$)$^-$ symmetrical stretching mode of non-bridging bonds in Q$^2$ units | [40] |
| 1352                   | P=O symmetrical stretching mode of non-bridging bonds in Q$^3$ units | [47] |

4. Conclusion
A series of glass composition with (60 - x) P$_2$O$_5$ - 10ZnO - 30PbF$_2$ - (x)Nd$_2$O$_3$ has been successfully prepared through melt-quenching technique. XRD spectra confirmed the amorphous nature of glass. The introduction of Nd$^{3+}$ ions into the glass network shows an increasing trend from 3.978 to 4.157 g cm$^{-3}$ which attributed to the NBO linkages formation in the network structure of the glass system. The molar volume shows the opposite behaviour from 41.949 to 41.073 cm$^3$ mol$^{-1}$ towards the density which indicates that the extra free spaces in the glass network are occupied by Nd$^{3+}$ ions. The FTIR main spectra revealed six prominent peaks in the spectrum can be observed in the 400-4000 cm$^{-1}$ wave-number. The Raman measurements show five prominent peaks are found in the frequency range of 600 - 1400 cm$^{-1}$ wave number within 1 cm$^{-1}$ resolution. Generally, as the Nd$_2$O$_3$ content is introduced to the glass system, there is a decrease of Q$^1$ chain terminator indicates that the glass network structure becomes more compact and cross-linked.
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References
[1] M. A. Algradee, A. E. B. Alwany, M. Sultan, M. Elgoshimy, and Q. Almoraisy, “Physical and optical properties for Nd2O3 doped lithium-zinc-phosphate glasses,” *Optik (Stuttg)*., vol. 142, pp. 13–22, 2017.
[2] L. Vijayalakshmi, K. Naveen Kumar, G. Bhaskar Kumar, and P. Hwang, “Structural, dielectric and photoluminescence properties of Nd3+ doped Li2O-LiF-B2O3-ZnO multifunctional optical glasses for solid state laser applications,” *J. Non. Cryst. Solids*, vol. 475, pp. 28–37, 2017.
[3] Y. B. Xiao, Y. Ji, J. L. Liu, and W. C. Wang, “Nd3+-doped mixed-anion fluoro-sulfo-phosphate glass for 1.06 μm solid-state laser,” *J. Non. Cryst. Solids*, vol. 522, p. 119586, 2019.
[4] A. Ichoja, S. Hashim, S. K. Ghoshal, I. H. Hashim, and R. S. Omar, “Physical, structural and optical studies on magnesium borate glasses doped with dysprosium ion,” *J. Rare Earths*, vol. 36, no. 12, pp. 1264–1271, 2018.
[5] H. Li, X. Liang, C. Wang, H. Yu, Z. Li, and S. Yang, “Structural aspects of calcium iron phosphate glass containing neodymium oxide,” *J. Mol. Struct.*, vol. 1067, pp. 154–159, 2014.
[6] Y. Ji, Y. B. Xiao, W. C. Wang, S. J. Huang, J. L. Liu, and Q. Y. Zhang, “Optical properties of Nd3+-doped fluoro-sulfo-phosphate glasses,” *J. Non. Cryst. Solids*, vol. 512, pp. 155–160, 2019.
[7] D. D. Ramteke, R. E. Kroon, and H. C. Swart, “Infrared emission spectroscopy and upconversion of ZnO-Li2O-Na2O-P2O5 glasses doped with Nd3+ ions,” *J. Non. Cryst. Solids*, vol. 457, pp. 157–163, 2017.
[8] C. E. Smith and R. K. Brow, “The properties and structure of zinc magnesium phosphate glasses,” *J. Non. Cryst. Solids*, vol. 390, pp. 51–58, 2014.
[9] S. N. S. Yaacob, M. R. Sahar, E. S. Sazali, Z. A. Mahraz, and K. Sulhadi, “Comprehensive study on compositional modification of Tb3+ doped zinc phosphate glass,” *Solid State Sci.*, vol. 81, pp. 51–57, 2018.
[10] H. Nurhafizah, M. S. Rohani, and S. K. Ghoshal, “Er3+:Nd3+ concentration dependent spectral features of lithium-niobate-tellurite amorphous media,” *J. Non. Cryst. Solids*, vol. 443, pp. 23–32, 2016.
[11] A. H. Hammad and A. M. Abdelghany, “Optical and structural investigations of zinc phosphate glasses containing vanadium ions,” *J. Non. Cryst. Solids*, vol. 433, pp. 14–19, 2016.
[12] R. Sk. Nayab, S. T., M. B. A., R. M. L., and J. C. K., “Optical spectroscopy, 1.06μm emission properties of Nd3+-doped phosphate based glasses,” *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 180, pp. 193–197, 2017.
[13] L. He, “Application of surface enhanced Raman spectroscopy to food safety issues,” *Ph.D. Thesis Univ. Missouri*, vol. 77, no. December, 2009.
[14] M. Premila, R. Rajaraman, S. Abhaya, R. Govindaraj, and G. Amarendra, “Atmospheric corrosion of boron doped iron phosphate glass studied by Raman spectroscopy,” *J. Non. Cryst. Solids*, vol. 530, p. 119748, 2020.
[15] S. A. M. Azmi, M. R. Sahar, S. K. Ghoshal, and R. Arifin, “Modification of structural and physical properties of samarium doped zinc phosphate glasses due to the inclusion of nickel oxide nanoparticles,” *J. Non. Cryst. Solids*, vol. 411, pp. 53–58, 2015.
[16] J. J. Hudgens, R. K. Brow, D. R. Tallant, and S. W. Martin, “Raman spectroscopy study of the structure of lithium and sodium ultraphosphate glasses,” *J. Non. Cryst. Solids*, vol. 223, no. 1, pp. 21–31, 1998.