Effect of Sodium Oxide and Sodium Fluoride in Gadolinium Phosphate Glasses Doped with Eu$_2$O$_3$ Content

S. Ravangvong$^1$, R. Rajaramakrishna$^2$, N. Chanthima$^{1,2}$, N. Sangwaranatee$^3$ and J. Kaewkhao$^{1,2}$

$^1$Physics Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University Nakhon Pathom, 73000, Thailand
$^2$Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom, 73000, Thailand
$^3$Applied Physics, Faculty of Science and Technology, Suan Sunandha Rajabhat University, Bangkok, Thailand

*E-mail: sunantasak@hotmail.com, jakrapong@webmail.npru.ac.th

Abstract. Sodium gadolinium phosphate oxide and sodium gadolinium oxyfluoride glasses doped with europium oxide were prepared by melt-quenching technique. The physical, optical properties of the glass samples were studied. The density, molar volume and refractive indices of the glass samples were carried out. Density and molar volume of oxide glass is more than oxyfluoride glass. The average phosphate to phosphate distance for oxide glass seems to be more than oxyfluoride glass. Polaron radius, inter-ionic radius shows 1.181 nm, 2.88 nm and 1.174 nm, 2.86 nm for oxide glass and oxyfluoride glasses respectively. Oxide electronic Polarizability and optical basicity of the oxide glass are lower than oxyfluoride glass. Theoretical optical basicity shows higher for oxide glass than oxyfluoride suggesting increase in covalency of the cation to oxygen bonds in oxide glass. Optical band gap were estimated and found to be 3.061 eV and 3.204 eV for oxide and oxyfluoride glass. Theoretical two photon absorption coefficient $\beta$ were evaluated and found to be 11.96 and 10.80 for oxide and oxyfluoride glasses respectively. Furthermore, the glasses were subjected to study for their luminescence properties of the oxide and oxyfluoride glass samples.

1. Introduction
Glasses have unique characteristics such as glass transition and insulators these are optically transparent [1]. Oxide glasses which contain alkali metal ions have been topic of interest due to their optical properties and optical transparency. [2-4]. Glass being amorphous solid exhibiting glass transition temperature [5]. Phosphate glasses are generally chosen for their low melting temperature, decrease in glass transition temperature, and elevated refractive indices [6-8].

Many fluorescent transitions of rare earth ions of practical importance are initiated from an excited level with a small energy gap in Eu$^{3+}$ ions [9-10]. Having electronic configuration [Xe]$^4$F$_6$ and intense emission of red (610 nm) color emitted due to hypersensitive $^4D_0\rightarrow^7F_2$ transition, Europium (Eu$^{3+}$) ions have been doped in many kinds of hosts for the development as laser gain medium in red laser device [11]. The luminescence of Eu$^{3+}$ ions enhance in the presence of Gd$^{3+}$ ions because small energy gap...
between Eu\(^{3+}\) and Gd\(^{3+}\) energy levels which permit the energy transfer between Eu\(^{3+}\) and Gd\(^{3+}\) ions [12]. The gadolinium ions have a half-filled 4f shell with a stable \(8S_{7/2}\) ground state and can be excited by UV light [13]. In this paper the research focuses on physical properties and optical band gap of the effect of sodium oxide and sodium fluoride in gadolinium phosphate glasses.

2. Experimental

Sodium gadolinium phosphate glasses (Na\(_2\)O: Gd\(_2\)O\(_3\): P\(_2\)O\(_5\)) glasses have the composition oxide and oxyfluoride 17Na\(_2\)O: 17Gd\(_2\)O\(_3\): 65P\(_2\)O\(_5\): 1Eu\(_2\)O\(_3\) (G1) and 17NaF: 17Gd\(_2\)O\(_3\): 65P\(_2\)O\(_5\): 1Eu\(_2\)O\(_3\) (G2) were prepared by melt-quenching technique. Glasses 2 samples were fixed doped with Eu\(_2\)O\(_3\) 1.00 mol\%. All chemical compositions were finely powder and then mixed in whole of composite. Each batch composition (about 20 g) was filled in high purity alumina crucible. All glasses were melted in an electrical furnace for 3 hours at 1200 \(^\circ\)C. Afterwards, the melts were quickly poured onto a preheated stainless steel mould, annealed at 500 \(^\circ\)C for 3 hours, and cooled down to room temperature, respectively. Finally, the glass samples were cut and finely polished to a thickness of 3 mm. Fig.1. Presents the photographs of polished glass samples. It is observed that with the addition of Eu\(_2\)O\(_3\), G1 and G2 glasses become good visibility and colorless.

The refractive index (n) was measured be Abbe refractometer with a sodium-vapor lamp as a light source and using mono bromonaphthalene (C\(_{10}\)H\(_7\)Br) as a contact liquid. The chemical bonds inside the glass matrix were investigated by FTIR spectra were obtained from Shimadzu, UV-3600 FTIR spectrophotometer in the spectral region 650-4000 cm\(^{-1}\). The optical absorption spectra was measured by UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) in the ultraviolet visible and near-infrared (UV-Vis-NIR) region from 190 to 2100 nm.

![Figure 1. Sodium gadolinium phosphate doped with Eu\(^{3+}\) in oxide and oxyfluoride glasses](image)

3. Results and Discussions

The analysis of physical properties are studied, the measurements are made at room temperature such as thickness (d), density (\(\rho\)) by Archimedes method using toluene as the immersing liquid as discussed in the literature [17-18]. It is observed from the table.1 that the density, molar volume and refractive index shows higher value for oxide glass than compared to oxyfluoride glass. The increase in density and refractive index is due to oxide glass contains excess of two Na atoms (Na\(_2\)O) than compared to oxyfluoride glass (NaF). Molar volume of oxide is higher due to ionic radii of O\(^{2-}\) (1.26Å) is higher than compared to oxyfluoride which contains F\(^-\) (1.19Å).
Table 1. Density, Molar Volume, Refractive index, Bond Strength and Bond length of Oxide and Oxyfluoride glasses.

| Glass Symbol | Density (g/cm³) | Molar Volume (cm³/mol) | Refractive Index (n) | Bond Strength (Na-O) (kJ/mol) | Bond Strength (Na-F) (kJ/mol) | Bond Length (Na-O) (Å) | Bond Length (Na-F) (Å) |
|--------------|----------------|-----------------------|----------------------|-------------------------------|-------------------------------|------------------------|------------------------|
| G1 - Oxide   | 3.3343         | 50.3682               | 1.5626               | 256.1                         | -                            | 1.964                  | -                      |
| G2 - Oxyfluoride | 3.3268         | 49.4603               | 1.5617               | -                             | 519                           | -                      | 1.926                  |

From table 2, the polaron radius and inter-ionic radius of oxide glass shows higher than oxyfluoride glass such trend is due to available alkali metal ions (Na⁺) concentration is more in oxide and hence attributed to breathe easy inside host matrix [18]. From table 2, the field strength of oxide glass shows lesser value than oxy-fluoride glass this is due to bond length of Na-O is greater than Na-F as shown in table 1. The number of available oxygen ions are more in oxide glass and hence they provide more volume suggesting that opening of phosphate network in the form of non-bridging oxygens which can be understood with Q⁰ terminology.

Table 2. Physical properties of oxide and oxyfluoride glasses

| Parameters                  | G1     | G2     |
|-----------------------------|--------|--------|
| Polaron Radius (nm)         | 1.181  | 1.174  |
| Inter-ionic Radius (nm)     | 2.880  | 2.863  |
| Field strength (×10²⁰)      | 2.596  | 2.627  |
| Number of Oxygen (NO²⁻)    | 3.96   | 3.79   |
| Cation Polarizability       | 0.476  | 0.446  |
| Oxide Polarizability        | 1.517  | 1.560  |
| Optical Basicity            | 0.569  | 0.600  |
| Optical Bandgap (eV)        | 3.061  | 3.204  |
| TPA (β)                     | 11.96  | 10.80  |
| Oxygen Packing Density      | 78.62  | 76.62  |

The UV-VIS absorption spectra of G1 and G2 glasses are shown in Fig. 2. The peaks centered at 361, 376, 393 and 463 nm wavelength are corresponding to transitions from the ground state ⁷F₀ to the excited ⁴D₂, ⁵G₄, ⁵L₆ and ⁵D₄, states respectively, while the peaks at 415 and 534 nm correspond to the transition from the thermally excited state ⁷F₁ to ⁴D₃ and ⁴D₁ states respectively. In present case the peaks related to ⁷F₀→⁴L₆ transitions is intense as compared to the rest of the peaks. Thus, electronic structure is fundamental to understand the nature of bonds that form the solid and thus many of the material properties. Low-frequency transitions are caused by interband transitions between the anion valence band and the cation conduction band.
Figure 2. UV-Vis absorption spectra of Eu$^{3+}$ doped in oxide and oxyfluoride glasses

The optical energy gap ($E_g$) for indirect transition is determined (with an error in the order of 0.02 eV) using Tauc’s method (Fig. 3) of extrapolating $(\alpha h\nu)^{1/2}$ versus photon energy in eV to zero were obtained and found to be 3.061 eV and 3.204 eV for oxide and oxy-fluoride glasses as shown in table 2.

![Optical band gap of Eu$^{3+}$ doped in oxide and oxyfluoride glasses](image)

Figure 3. Optical band gap of Eu$^{3+}$ doped in oxide and oxyfluoride glasses

Two-photon absorption (TPA) is one of the most basic radiation-matter interaction mechanisms. Two-photon absorption can place fundamental limitations on the waveguide all-optical switching devices [3, 17]. The nonlinear absorption coefficient or the two-photon absorption coefficient, $\beta$, along with bandgap energy, $E_g$, has been described by a universal expression for alkali metal-containing oxide and oxyfluoride glasses and it is given by the below equation [18].

$$\beta \text{ (cm/GW)} = 36.76 - 8.1E_g \text{ (eV)}$$

The TPA coefficient of a photonic glasses, such sodiumoxide and sodium fluoride phosphate glass, formed by acidic oxides (as $P_2O_3$) becomes weaker in glasses produced by a mixture of acidic and basic oxides (as NaO/NaF). The TPA ($\beta$) value decreases with addition of fluoride ions than oxygen ions.
Such decrease in the value is due to the replacement of $O^{2-}$ (1.26Å) with higher ionic radii $F^{-}$ (1.19Å) lower ionic radii which could decrease the nonlinear optical absorption coefficient of the glass.

4. Conclusions

In this work, sodium gadolinium phosphate glass (G1) and oxyfluoride (G2) glasses doped with europium (III) oxide were prepared by melt-quenching technique and investigated their physical and optical properties to determine the potential use for luminescence materials. The increase in density and refractive index of the oxide glass is found to be due to excess of Na atoms ($Na_2O$) presence than compared to oxyfluoride glass ($NaF$). The highest peak in absorption spectrum centered at 393 nm ($^7F_0 \rightarrow ^5L_6$) in UV-Vis region compared to other peaks. TPA ($\beta$) decreases with replacement of $O^{2-}$ by $F^{-}$ suggesting that the nonlinear absorption coefficient of glass is less in oxyfluoride glass. Furthermore, these oxide (G1) and oxyfluoride (G2) glasses will be studied for photoluminescence and energy transfer phenomenon for their potential candidature in solid state device applications.

Acknowledgements

The authors would like to thanks Physics Program, Faculty of Science and Technology and Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University (NPRU) for supporting this research.

References:

[1] Raja Ramakrishna Raja navaneetha krishna, Chananya Wongdeeying, Patarawagee Yasaka, Pruittipol Limkitjaroenorn, Narong Sangwaranatee, and Jakrapong Kaewkhao, *Journal of Metals, Materials and Minerals*, Vol.28 No.2 pp.47-54, 2018
[2] R. Rajaramakrishna, Y. Ruangtaweep, N. Sangwaranatee, J. Kaewkhao, *Journal of Non-Crystalline Solids* 521 (2019) 119522.
[3] R. Rajaramakrishna, Safakath Karuthedath, R.V. Anavekar, H. Jain, Journal of Non-Crystalline Solids 358 (2012) 1667–1672.
[4] Rajagukguk, J., Hidayat, R., Djamal, M., Ruangtaweep, Y., Horprathum, M. and Kaewkhao, J., 2016. *Structural and Optical Properties of Nd3+ Doped Na2O-PbO-ZnO-Li2O-B2O3 Glasses System*. In Key Engineering Materials (Vol. 675, pp. 424-429). Trans Tech Publications.
[5] R. Rajaramakrishna and Jakrapong Kaewkhao, UNNES International Conference on Research Innovation and Commercialization 2018,KnE Social Sciences, pages 796–807.DOI 10.18502/kss.v3i18.4769
[6] R. Lakshmikantha, R. Rajaramakrishna, R.V. Anavekar, and N.H. Ayachit, *Can. J. Phys.* 90: 235–239 (2012).
[7] M. Shoaib, G. Rooh, N. Chanthima, R. Rajaramakrishna, H.J. Kim, C. Wongdeeying, J. Kaewkhao, *Optical Materials* 88 (2019) 429–444
[8] Rajagukguk, J., Situmorang, R., Djamal, M., Rajaramakrishna, R., Kaewkhao, J. and Minh, P.H., 2019. *Structural, spectroscopic and optical gain of Nd3+ doped fluorophosphate glasses for solid state laser application. Journal of Luminescence*, 216, p.116738.
[9] K. Kirdsiri, R. Rajaramakrishna, B. Damdee, H.J. Kim, N. Nuntawong, Mati Horphathum, J. Kaewkhao, *Solid State Sciences* 89 (2019) 57–66.
[10] Rajagukguk, J., Kaewkhao, J., Djamal, M., Hidayat, R. and Ruangtaweep, Y., 2016. *Structural and optical characteristics of Eu3+ ions in sodium-lead-zinc-lithium-borate glass system*. Journal of Molecular Structure, 1121, pp.180-187.
[11] I. Khan, G. Rooh, R. Rajaramakrishna, N. Sirsittapakun, H.J. Kim, J. Kaewkhao and K. Kirdsiri, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 210 (2019) 21–29.
[12] M. Shoaib, G. Rooh, N. Chanthima, R. Rajaramakrishna, H.J. Kim, C. Wongdeeying, J. Kaewkhao, *Optical Materials* 88 (2019) 429–444.
[13] I. Khan, G. Rooh, R. Rajaramakrishna, N. SirsittiPokakun, H.J. Kim, C. Wongdeeying, J. Kaewkhao, Journal of Luminescence 203 (2018) 515–524.

[14] R. Rajaramakrishna, B. Knorr, V. Dierolf, R. V. Anavekar, H. Jain, J. Lumin., 156 (2014) 192–198.

[15] S. Kaewjaeng, S. Kothan, W. Chaiphaksa, N. Chanthima, R. Rajaramakrishna, H.J. Kim, J. Kaewkhao, Radiation Physics and Chemistry 160 (2019) 41–47.

[16] K. Kirdsiri, R. Raja Ramakrishna, B. Damdee, H.J. Kim, S. Kaewjaeng, S. Kothan, J. Kaewkhao, Journal of Alloys and Compounds 749 (2018) 197-204.

[17] R. Rajaramakrishna, Chatree Saiyasombat, R.V. Anavekar, H. Jain, Journal of Non-Crystalline Solids 406 (2014) 107–110.

[18] Manal Abdel-Baki, Fathy A. Abdel-Wahab and Fouad El-Diasty, Journal of Applied Physics 111, 073506 (2012).