Impact of Nd_2O_3 on physical properties of lead borate glass system

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Abstract: The Nd_2O_3 doped lead borate glass (BPZN:Nd) with composition $45B_2O_3$-(40-x)PbO-11ZnO-$4Na_2O$-xNd_2O_3 (x=0; 0.5; 1.0; 1.5; 2.0; 2.5) mol% were fabricated using melt quenching method at 950°C for 35 minutes. The characterization of physical properties of lead borate glasses doped with Nd_2O_3 were measured from their density (ρ) based on the Archimedes principle. The others physical parameters such as: molar volume (Vm), Oxygen Packing Density (OPD), Polaron radius (r_p), Ionic radius (r_i), Field Strength (F), Molar refraction (R_m), and Metallization criterion (M_n) were calculated using equation which derived from the density. According to the measurement, the density of glasses decreased from 5.774 to 4.527 gr/cm^3 while, molar volume oppositely increased from 23.17 to 30.18 cm^3/mol due to smaller atomic mass of Nd (144.24) rather than Pb (207.2). Along with the increase of molar volume, there were decreasing of the OPD, r_p (1.731 −1.095) Å and the r_i (4.296−2.717) Å of glasses. Meanwhile, the F and M_n increased as a result of the reduction r_p and r_i. The investigation of R_m also shows an increasing trend due to addition of the Nd_2O_3 concentration.

Keyword : Lead borate glasses, Metalization, OPD, Polaron radius.

1. Introduction

Glass is a material that has high transparency, high chemical resistance, and excellent thermal and optical properties (Razali et al., 2012; Hu et al., 2017). Borate based glass (B_2O_3) has been recognized as one of the best glass-forming material that can form glass at low melting point, with high transparency, high thermal stability, and good rare earth ion solubility (Mahamuda et al., 2013; Mhareb et al., 2014; Annaporani et al., 2016, Fausta et al., 2020, Saraswati et al., 2021, Marzuki et al., 2021). The structure of borate glass does not originate from the random distribution of trigonal BO_3 and tetrahedral BO_4, but the collection of these units forms well-defined and stable borate structures, such as: diborate, triborate, and tetraborate., which are three-dimensional networks (Wagh et al., 2015). On the other hand, the drawback of borate glass is its high phonon energy (Nor et al., 2017; Kaur et al., 2021). Its known that glass systems with low phonon energy are particularly suitable for high-efficiency lasers and fibre amplifiers (Amer et al., 2022). Glass which containing Heavy Metal Oxides (HMO) as a modifier on its matrix can reduce it phonon energy (Chen et al., 2003; Dumbaugh et al., 2005). The contribution of HMO such as PbO in glass formation increases the chemical stability and density (Elsad et al., 2012). Others metal oxides like ZnO can modify structural, physical, and chemical resistance of glass (Abdel et al., 2012).

Glass containing heavy metal ions and rare earth ions has received great attention in recent years (Ali et al., 2018). Glass with rare earth ion (lanthanide) doping is widely used in various applications such as: solid-state lasers, sensors, optical switches, telecommunication, part of electronics device, automotive, fibre optic cables, chemical laboratory equipment, flat panel devices as television screens, and medical applications. Therefore, glass doped with rare earth ions becomes attractive research to deeply investigate (Elkhoskhany et al., 2019). Among the Lanthanide ions, Nd^{3+} is one of the most extensively studied ions for solid-state lasers due its high emission at useful wavelengths at 1064 nm (James et al., 2020; Rajaramakrisna et al., 2021). High hardness and good chemical resistance make Neodymium widely favoured as one of glass doping material (Algradee et al., 2017).

It has been reported in a study by Algradee et al. (2017) regarding the physical properties of glass lithium-zinc-phosphate-doped Nd_2O_3 obtained densities in the range of 3.155-3.265 gr/cm^3. This paper presents the effect of the addition of Nd_2O_3 on the physical properties of lead borate glass with general composition: B_2O_3-PbO-ZnO-Na_2O- Nd_2O_3 which is expected posses greater density. Physical parameters i.e. density, molar volume, ion concentration, polar radius, ion spacing, field strength, oxygen packing density, molar refraction, and metallization are calculated using derived formula from obtainable density.

2. Experimental

Lead borate glasses were fabricated with melt quenching methods with chemical composition: $45B_2O_3$-(40-x)PbO-11ZnO-$4Na_2O$-xNd_2O_3, x varying from 0, 0.5, 1.0, 1.5, 2.0, 2,5 mol%. The raw materials were weighted and mixed using mortar until completely homogeneous. The mixture then placed in an alumina crucible and melted using electrical furnace at 950°C for 45 minutes. The casting process was carried out by pouring glass melted into a rectangular brass mold which has been previously heated inside an oven at 250°C. The obtained glasses were annealed at 275°C for 8 hours to remove thermal shock and mechanical stress.

Identification of the physical and properties of glasses to obtain its physical parameters as the main reference for the manufacturing glasses in various applications. The characterization of the physical properties was obtained by measuring the density (ρ) based on the Archimedes principle. Density was measured using a pycnometer at room temperature by applying Equation (1):

$$\rho_g = \frac{m_{g+p} - m_p}{(m_{g+p} - m_p) - (m_{g+d+p} - m_{d+p})} \rho_d \tag{1}$$

Where ρ_g, ρ_d, m_p, m_{g+p}, m_{d+p}, m_{g+d+p} are density of the glass, density of the water, pycnometer mass filled with aquades, pycnometer mass filled with aquades and glass. Other parameters of the physical properties glass can be derived from density values, including molar volume (V_m), concentration of Nd^{3+} ions in glass (N_{Nd}), Polaron radius (r_p), Ionic radius (r_i), Field Strength (F), Oxygen Packing Density (OPD), Molar Refraction (R_m), and Metallization criterion (M_n).

The volume molar of the glass can be calculated by using the following Equation (2):

$$V_m = \frac{\sum(n_i.X_i)}{\rho_g} \tag{2}$$

With n_i is mol fraction of each component and X_i is molecular weight of each component.

The ionic concentration of Nd^{3+} in each of the glass can be known by Equation (3):

$$N_{Nd} = \mathrm{N_A}\frac{\mathrm{n}_{Nd}\,\rho_\mathrm{g}}{M_w} \tag{3}$$

With N_A is Avogadro constanta ($6{,}023\times10^{23}$ mol^{-1}) and n_{Nd} is mol fraction of Nd_2O_3. Polaron radius and ionic radius can be calculated using Equation (4) and (5):

$$r_p = \frac{1}{2}\left(\frac{\pi}{6\,N_{Nd}}\right)^{0.5} \tag{4}$$

$$r_i = \left(\frac{1}{N_{Nd}}\right)^{\frac{1}{3}} \tag{5}$$

The vakue of Nd_2O_3 cation is Z, so the field strength of glass that containing Nd_2O_3 can be known by Equation (6):

$$F = \frac{Z}{{r_p}^2} \tag{6}$$

OPD of the glass can be calculated by Equation (7):

$$OPD = 1000\frac{\rho_g}{M_w}N \tag{7}$$

Molar refraction was calculated by determining the cation polarizability and oxide ion polarizability of each glass component obtained from Dimitrov et al. (2010). Calculation of molar refraction using Equation (8):

$$R_m = 2.52\,\alpha_m \tag{8}$$

Meanwhile, the criteria for metallization of the material (M_n) can be determined using Equation (9):

$$M_n = 1 - \left(\frac{R_m}{V_m}\right) \tag{9}$$

3. Result & Disscussion

All obtained physical parameters can be used to explain the effect Nd2O3 addition on changes in the physical properties of lead borate glass system. The physical parameter was tabulated in Table 1.

Table 1. Parameter physical properties from BPZN glass with Nd_2O_3 variation

Parameter physical properties	**% Nd_2O_3**					
	0	**0.5**	**1**	**1.5**	**2**	**2.5**
Densitas (gr/cm^3)	5.774	5.629	5.323	4.902	4.787	4.527
Vm (cm^3)	23.17	23.87	25.35	27.64	28.42	30.18
N_{Nd} (× 10^{22} ion/cm^3)	0	1.261	2.376	3.268	4.238	4.988
r_p (Å)	0	1.731	1.402	1.26	1.156	1.095
r_i (Å)	0	4.296	3.479	3.128	2.868	2.717
F (× 10^{15}) (cm^{-2})	0	1.626	2.479	3.066	3.646	4.065
OPD (g.atom/l)	85.445	83.368	78.894	72.724	71.071	67.263

Density and molar volume of glasses doped with Nd_2O_3 is shown in Figure 1. Based on the Figure 1., the density value decreased from 5.774 - 4.527 gr/cm^3, while the molar volume of glass increased from 23.17 - 30.18 cm^3/mol with increasing of Nd_2O_3 concentration. The decrease in density may caused by greater the atomic mass of Pb (207) rather than Nd (144). The same research which reported by Mahamuda et al. (2013) replacing the Bi_2O_3 with Nd_2O_3 in composition 20ZnO-10Al_2O_3-(10-x)Bi_2O_3-60B_2O_3-$x$$Nd_2O_3$ was reduced the density from 3.298 to 3.265 gr/cm^3. The ionic radius of Nd^{3+} (229 pm) which larger than Pb^{2+} (133 pm) also resulting Nd^{3+} ions not able to fill the spaces inside glass network optimally. So, the glass samples become less dense.

The molar volume of glasses is in contrast to the density. The increase in molar volume is related to the increasing of Non Bridging Oxygen (NBO) in the glass. The addition of Nd_2O_3 allows to formation of NBO which will break the atomic bonds of the glass host and make the space of the glass component structure is more empty (Alazoumi et al., 2018). This causes the glass sample to be less dense. In addition, an increase in molar volume can be associated with an increase of bond length or interatomic spacing between atoms of the glass network (Wagh et al., 2015).

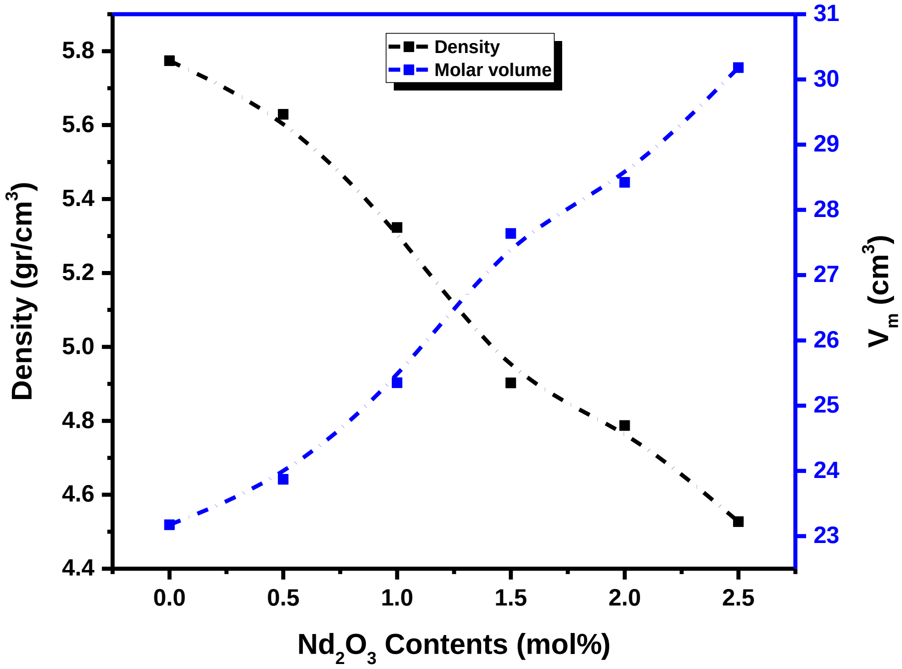

Figure 1. Density and molar volume of BPZN Glass with Nd_2O_3 variation

Based on Figure 2. is observed that the increase of concentration Nd^{3+} ions (1.261-4.988) ($\times 10^{22}$ ions/cm^3) involve the calculation of the ionic radius which decreases from 4.30 Å to 2.72 Å, thus allowing the distance between ions on the glass become smaller. From Equation (6) it can be seen that the polaron radius is inversely to the field strength. Calculation of polaron radius shows that decrease from the range of 1.73 Å to 1.09 Å. The polaron radius and ionic radius, which decrease with increasing of Nd_2O_3, lead to a decrease of the Nd-O bond length so the Nd-O bond strength increases and produces a greater field strength (Aljewaw et al., 2020). The significant increase in field strength from 1.626 - 4.065 ($\times 10^{15}$ cm^{-2}) is due to stronger bond between Nd^{3+} ions and B ions (Wu et al., 2014).

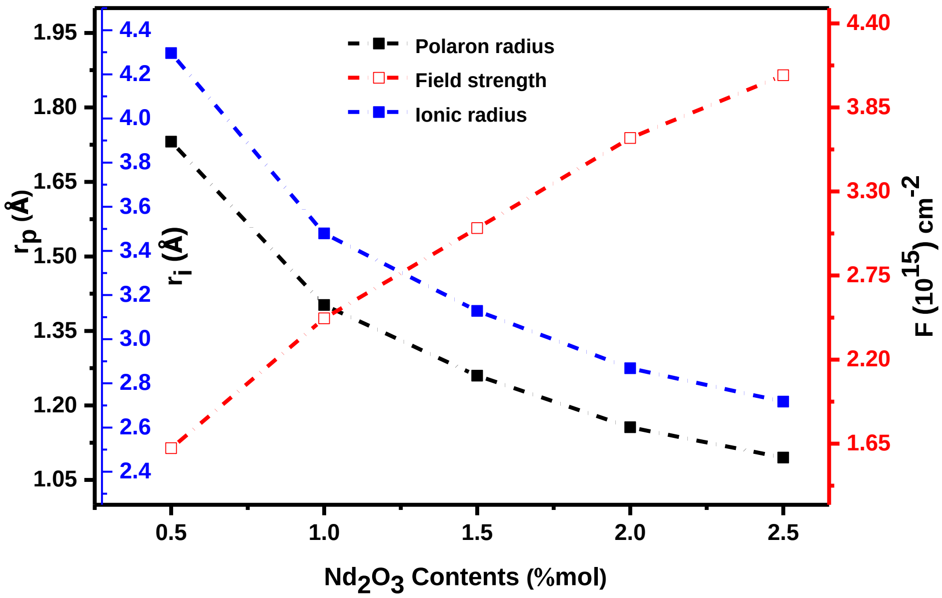

Figure 2. Polaron radius, ionic radius, and field strength of BPZN glass doped Nd_2O_3

Oxygen packing density is describe of the compactness and rigidity of the glass structure. Based on Figure 3, shows a decrease in OPD from the range of 85.445 to 67.263 mol/cm^3 by increasing Nd_2O_3. This is an effect on the formation of NBO which expanding the glass structure, related to glass molar volume (Nasuha et al., 2021). Therefore, glass structure becomes less dense and the OPD value decreases and directly reduce the glass density.

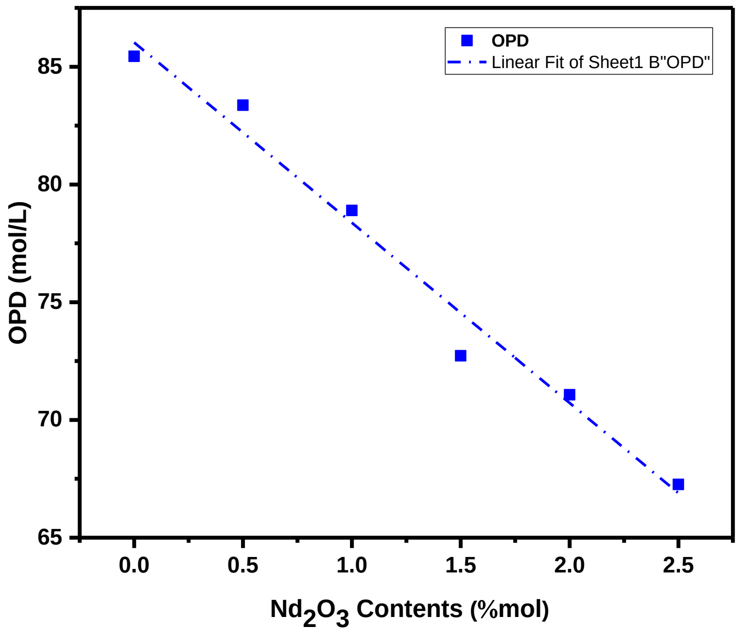

Figure 3. OPD of BPZN glass with addition of Nd_2O_3

Table 2. Molar refraction and metallization of BPZN glass on Nd_2O_3 concentrations

% Nd_2O_3	**R_m (cm^3/mol)**	**Mn**
0	12.639	0.455
0.5	12.678	0.469
1	12.718	0.498
1.5	12.757	0.538
2	12.797	0.550
2.5	12.836	0.575

The results of the molar refraction and metallization criterion of BPZN:Nd glasses are presented in Table 2. The molar refraction increased from 12.639 - 12.836 cm^3/mol with the addition of Nd_2O_3. It causes by the increasing amount of NBO which has greater polarizability (Halimah et al., 2020). Metallization criterion is a parameter which related to consideration of the metal or non-metal type of the glass. Glass among the metal if the metallization value is > 1 and it among to non-metallif metallization < 1. The calculation shows that the metallization criterion of BPZN:Nd glass in this study ranges from 0.455 - 0.575, which mean all glasses have non-metal properties.

4. Conslussion

B_2O_3-PbO-ZnO-Na_2O glass with various doped Nd_2O_3 (x = 0; 0.5; 1; 1.5; 2; 2.5 mol%) has been successfully fabricated using the melt quenching method. The characterization of the physical properties of glass were analyzed based on the derived of density measurements. The results shows that the addition of Nd_2O_3 to BPZN glass reduced the density from 5.774-4.527 gr/cm^3 and increase the molar volume from 23.17-30.18 cm^3. The physical properties such as polaron radius, ionic radius, and OPD have decreased. Meanwhile, the field strength, molar refraction, and metallization criterion are increased.

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