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PHYSICAL AND STRUCTURAL PROPERTIES OF Nd_2O_3 DOPED BORATE GLASS

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ABSTRACT

The Nd^{3+} doped borate glass system with composition $x$$Nd_2O_3$-5MgO-20ZnO-(75-$x$) B_2O_3 with x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 successfully been prepared by melt-quenched technique. The physical properties by mean of density and molar volume are well determined. From the results, the glass densities are found to increase from 3193 kgm^{-3} to 3530 kgm^{-3}. The increment in density implies that an addition of Nd_2O_3 with higher atomic masses than B_2O_3 tend to increase the packing density of the glass structures since the atomic masses of B_2O_3 and Nd_2O_3 are 69.62 and 336.42 respectively. From the density values obtained, the molar volume of glasses was calculated. It is found that the molar volume of these glasses decreases slightly from 22.50 cm^3 to 22.24 cm^3 with respect to Nd_2O_3 content. Meanwhile, the structural properties have been determined by using Fourier transform infrared (FTIR) spectroscopic techniques. From the experiment, it is observed that there are several significant peaks which correspond to the structural bonding of the glass in a range of 650 – 4000 cm^{-1}. The peaks found are consistent with the stretching and bending vibration of the glass structure as predicted.

Keywords: borate glass; glass density; molar volume; FTIR;

INTRODUCTION

Borate glass has attracted extensive attention in the past several years because of its technological and industrial interests for their use in photonics, and optoelectronic applications. In comparison with other conventional glasses, borate glass is a most recently studied due to some interesting features such as low melting temperature, wide glass formation region, high refractive index and good radiation shielding for x-rays[1-3]. It is also well known to be good in mechanical strength, chemical durability, stable against atmospheric moisture, low melting temperature and good in corrosion resistance. Therefore these glasses have wide applications in the fields of electronics, nuclear and solar energy technologies and acoustic-optic devices.

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Borates glasses have been widely used for optical lenses with high refractive index and low dispersion characteristics. The ZnO–PbO–B_2O_3 glasses have been characterized for a strong tendency for phase separation and are used in glass solders for sealing CTV bulbs, IC packages, and glass discharge tubes [6]. It also possesses excellent IR transmission [7] and high refractive index, [8, 9]. The addition of ZnO also makes them suitable to be used in plasma display panels for high quality and performances for the simple reason that these glasses possess high dielectric breakdown strength with room temperature dielectric constant around 15, low thermal expansion coefficient and good transparency [10,11]. Incorporation of rare earth such as Er^{3+} or Nd^{3+} into borate glass is responsible for high IR transmission ability [12], thus it has been a key to the development of many optical devices such as infrared lasers, IR-visible upconverters, fibre and waveguide amplifiers for optical transmission network [13].

Mohan et al [17] have investigated the effect of the Nd^{3+} to density of borate glass and found the density is increase with increasing of Nd^{3+} while the molar volume shows opposite trend. J.E Shelby [4] reported that the boron atom in borate crystals and glasses usually coordinates with either three or four oxygen atoms forming [BO_3] or [BO_4] structural units. These two fundamental units can be arbitrarily combined to form either the so-called super-structure or different B_xO_y structural groups such as boroxol ring, pentaborate, tetraborate and diborate groups. It is known that pure B_2O_3 glass consists mainly of boroxol ring $B_3O_{9/2}$ with three-coordinated BO_3 units; thus, modification by alkali will alter its structure [5]. Regarding the uniqueness of borate glass structure and its wide application, therefore in this work a series of Nd^{3+} doped borate glass are being prepared by using melt-quenching technique in order to study the effect of Nd^{3+} concentration to their physical and glass structure since not much research has been done nor reported elsewhere.

EXPERIMENTAL METHOD

Physical properties

The Nd^{3+} doped borate glass of Nd_2O_3-MgO-ZnO-B_2O_3 glass system is prepared by melt-quenching technique. Batches of 15g were prepared from certified reagent grades of B_2O_3 (99.95% purity), MgO (97%), ZnO (98% purity), and Nd_2O_3 (99.995%). Appropriate amounts of chemicals were weighed by using an electronic balance with an accuracy of ±0.001 g. The chemicals were firstly mixed thoroughly in a platinum crucible before being heated at 1000 ^oC for half an hour. After the batch was completely melted, the melts was cast onto the preheated stainless steel plate followed by annealing at 400 ^oC for 5 hours before allowed to cool down to room temperature in order to avoid the sample from breaking through residual stress. The density of glass samples at room temperature was measured by using Electronic densitometer MD-3005 based on Archimedes principal with distilled water as the immersion fluid. The minimum density resolution of the densitometer is 0.001 kgm^{-3}. The molar volume is calculated as:

$$V_m = \frac{\Sigma M_i}{D} \qquad (1)$$

Mi denotes the molar mass of the glass, where $M_i = C_i A_i$. Here C_i and A_i are the molar concentrations and molecular weight of the *i* th component, respectively, and *D* is the calculated density.

For the structural analysis, infrared spectroscopy was carried out at room temperature in the region 650–4000 cm^{-1} using the Pelkin Elmer spectrometer. In this analysis the attenuated total reflectance (ATR) method is used in the range from 650–4000 cm^{-1}. For each sample the spectrum represents of 20 scans.

RESULTS AND DISCUSSION

The samples obtained are in good quality as visualized. From the observation, it is found that the presence of Nd^{3+} ions in the glass system tend to change the color of the glass from light purple to dark purple. It is also shows clear and transparent behavior in nature. The samples are seen to be non-hygroscopic which indicate a relatively higher chemical durability since they show no sign of devitrification.

Table 1: Density and Molar volume of the Nd^{3+} doped MgO-ZnO-B_2O_3 glass.

x	mol%			Density,	Molar	
	B_2O_3	MgO	ZnO	ρ (gcm^{-3})	volume, V_m	Remarks
0.5	74.5	5.0	20.0	3.193	22.50	Light purple
1.0	74.0	5.0	20.0	3.249	22.52	Light purple
1.5	73.5	5.0	20.0	3.312	22.37	Purple
2.0	73.0	5.0	20.0	3.410	22.24	Purple
2.5	72.5	5.0	20.0	3.477	22.20	Dark purple
3.0	72.0	5.0	20.0	3.530	22.24	Dark purple

As tabulated in Table 1, the glass density increases from 3193 kgm^{-3} to 3530 kgm^{-3} with respect to mol% of Nd^{3+} content. As been observed in Figure 1, the increasing trend of density implies that an addition of Nd_2O_3 with higher atomic masses than B_2O_3 tend to increase the packing density of the glass structures since the atomic masses of B_2O_3 and Nd_2O_3 are 69.62 and 336.42 respectively. This trend of results also has been found by Sudhakar *et.al* [14] in their works. Meanwhile, the molar volume of glasses was calculated from the density values obtained. As depicted from Table 1 and Figure 1, it is found that the molar volume of these glasses decreases slightly from 22.50 cm^3 to 22.24 cm^3 with respect to Nd_2O_3 content.

An addition of 0.5 mol% to 3.0 mol% of Nd^{3+} to borate glass might cause some changes in the glass structure as the results of molar volume show decrement trend. It might be due to the ability of B^{4+} to change into B^{3+} as the glass coordination number changes from 4 to 3. The changing of coordination number is a factor that might cause a decrement in molar volume [15, 16]. In general, the decrease of molar volume indicates a decrease in the interatomic distances. Incorporation of Nd^{3+} is believed to alter the glass structure by creating more BO (bridging oxygen) that increase the glass

compactness thus enhance the rigidity of the glass. [17].

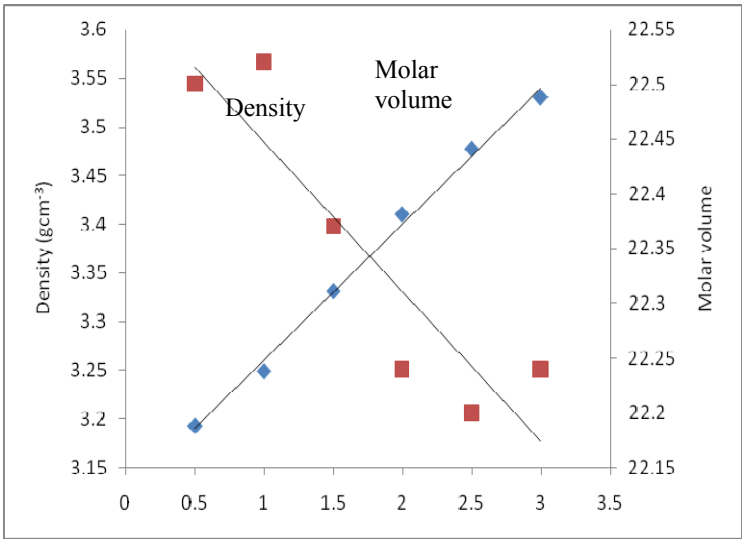

Figure 1: Density of Nd^{3+} and molar volume of Nd^{3+} doped MgO-ZnO-B_2O_3 glass

Structural properties

The infrared absorption spectra of the glass have been measured to obtain possible changes of vibrational spectra. The IR spectra of $x$$Nd_2O_3$-5MgO-20ZnO-(75-$x$)$B_2O_3$ glass as shown in Figure 2. Five significant absorption bands at around 3927 -3486 cm^{-1}, 2357-2255 cm^{-1}, 1778-1708 cm^{-1}, 1572-1142 cm^{-1}, 1142-788 cm^{-1} region have been observed. The summary of peak position is shown in Table 2. From the result, band which centered at 3734 cm^{-1} is originating from OH-groups as reported [7]. This group is originates from the water present in the raw material and the atmosphere in which the glass is produced. Meanwhile the peak centered at 2304.19 cm^{-1} are attributed from the carbon stretching since diamond has been used as a probing material in ATR method. This might be due to diamond has a high transmittance throughout the mid-infrared spectrum [18, 19]. Whereas, the absorption peak observed at 1738 cm^{-1} region is correspond to the hydroxyl-metal bond as well as the hydroxyl-hidrogen bond stretching vibration [20].

The absorption band centered at 1572-1142 cm^{-1} region is attributed to B-O bond stretching vibration involving the linkages between oxygen and other different groups, as well as the B-O bridging between B_3O_6 rings and BO_3 triangle [5,21,22]. However the incorporation of Nd^{3+} from 0.5 mol % to 2.5 mol % into glass structure seems to shift the absorption peaks toward lower wavelength from 1334.33 cm^{-1} in x = 0.5 to 1334.6 cm^{-1}, 1324.12 cm^{-1}, 1290.94 cm^{-1}, 1289.19 cm^{-1} respectively. The shift is might be attributed to the stretching vibration of BO_3 unit with increment of Nd^{3+} content [7]. Meanwhile, band in the 1142-7883 cm^{-1} region is assign to the B-O bond stretching of tetrahedral BO_4 unit [6, 23]. This band also been observed to shift toward lower wavenumber with the increment of the Nd_2O_3 from 0.5 mol % to 2.5 mol %. The peak

are shifted from 976.58 cm^{-1} to 913.71 cm^{-1}, 913.71 cm^{-1}, 875.29 cm^{-1}, 842.10 cm^{-1} which attributed to the stretching vibration of BO_4 unit. The peaks shifting are might be due to the formation of BO_3 and BO_4 unit with respect to Nd^{3+}. It might be due to fact that Nd^{3+} acts as a modifier by modifying the glass structure. Beside that the band of BO_4 was observed to shift larger than BO_3 band which could be due to higher formation of BO_4 compare to BO_3. The band of BO_4 was observed to shift larger than BO_3 band might be due to BO_3 unit converted to BO_4 unit yielding the open structure of glass [18].

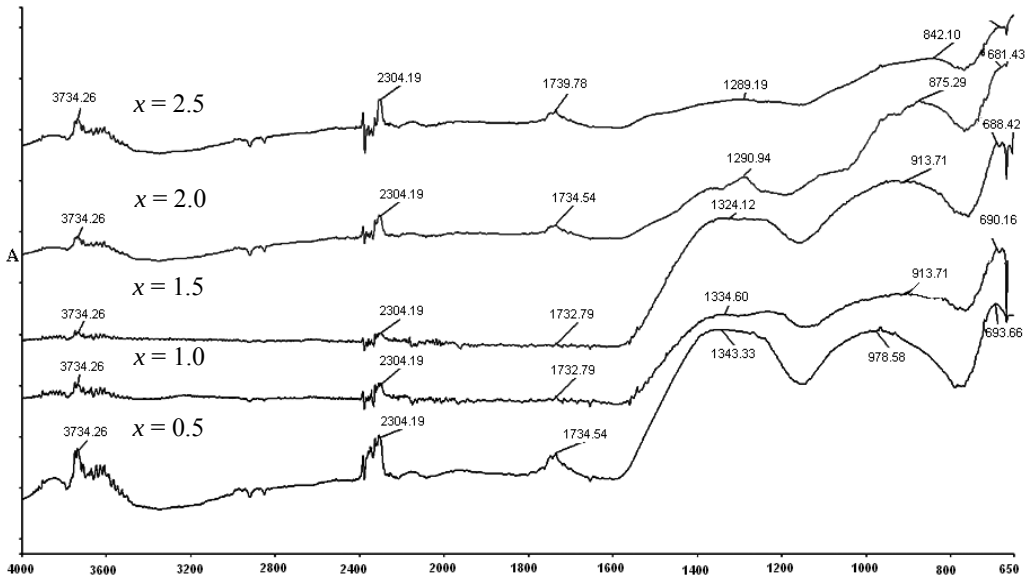

Figure 2: The infrared spectra of xNd_2O_3-5MgO-20ZnO-(75-x) B_2O_3 glass

Table 2: Assignment of the infrared absorption band on the studied glass

Peak position(cm^{-1})	Assignment
1) 3927 -3486	OH-group
2) 2357-2255	Carbon stretching
3) 1778-1708	M-OH group
4) 1572-1142	BO_3 stretching vibration
5) 1142-788	BO_4 stretching vibration
6) 690	B-O-B bending vibration

Finally the peak which arise around 690 to 681 cm^{-1} regions is correspond to the bending of B-O-B linkages in the borate network [5, 24-26]. The vibration of metal cation such as Zn^{2+} and Mg^{2+} normally occur at 420 cm^{-1}. However, in our instrument

the range of the absorption band is only within 4000 to 650 cm^{-1} by using ATR method therefore it is impossible to detect metal cation in our sample.

CONCLUSION

The physical and structural properties of Nd^{3+} doped borate glass have successfully been investigated. The density of glasses is found to increase with respect to mol% of Nd^{3+}. The inversely proportional results are shown by the molar volume which decreases as the mol% of Nd^{3+} increases. The increment of Nd_2O_3 content into the glass structure tends to increase the density as the BO_3 and BO_4 are formed. From the FTIR spectra analysis it is can concluded that, the main group of BO_3 and BO_4 is become as the network structural group. The addition of rare earth seems to alter the glass network by the formation of BO_4 from BO_3.

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