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Physical Optical Properties of 20CaO-(80-x)B_2O_3-xZnO Glass System

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Abstract

The calcium borate added with zinc oxide glass samples with chemical formula 20CaO-(80-x)B_2O_3-xZnO (where x=0, 5, 15 and 20 mol%) were prepared by the melt quenching technique. Glass samples were melted at 1,200°C for 3 h and annealed at 500°C for 3 h. Glasses density decreases, while molar volume increase with increment of ZnO concentration. Based on the transmission and absorption spectra obtained, the direct and indirect optical band gap, as well as the Urbach energy were calculated. The optical band gap expand with increasing of ZnO concentration that probably represents the NBOs located in glass network. Urbach energy increase with increasing of ZnO concentration due to the defects produced within the localized states. The optical basicity and polarizability of glass samples have been investigated in this work.

Keywords: Glass; Physical properties; Optical properties; Optical band gap; Optical basicity; Polarizability

Introduction

Glass is a promising host to investigate the influence of chemical environment on the optical properties. Many researchers have proposed the use of glass materials as optical applications and ionizing radiation detectors in different fields due to its many valuable properties such as easy in handling, chemical inertness and rigidity etc. In addition, glass can be in contact or very close to the exposed persons and therefore, can be used as emergency dosimeters(1,2). Borate compounds have been widely studied due to their features as glass formers and also on account of being very advantageous materials for radiation dosimetry applications(3). The glass structure of zinc borate has not been sufficiently investigated, zinc ion is known as a network modifier and the structure might be similar to that of alkali borate glass(4). Generally, in these glasses, there are two major composition-dependent structural changes: the disintegration of the six-membered boroxol rings into non-ring BO_3 units, and the dissociation of the BO_4 species into symmetric BO_3 units with three B–O–B linkages and NBOs(5). Glasses with 60 mol% ZnO concentration have been successfully prepared without deteriorating the glass-forming ability(6). Adding calcium element can increase intensity of luminescence emission of glass(7). Study of structure, physical and optical properties of many glass systems have been interested, especially in borate glass because of good properties in various applications(8). When filling a heavy modifier, will cause a physical and optical change. Therefore the effect of ZnO concentration will be interesting. The aim of this work is to study the the physical and optical properties of the 20CaO-(80-x)B_2O_3-xZnO (where x = 0, 5, 15 and 20 mol%) glass system. The energy gap was estimated and the optical basicity and polarizability were calculated. Electronic polarizability is related to many properties of materials such as refraction, optical nonlinearity and optical basicity(9-11).

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Experimental

The glasses used in this work were prepared with the composition in mol%; 20CaO-(80-x)B_2O_3-xZnO (where x = 0, 5, 15 and 20 mol%) were prepared by the melt quenching technique. For preparation of these glass samples, the high purity chemicals are CaO, H_3BO_3 and ZnO were mixed in high purity alumina crucible for total weight 10 g. These glass compositions were heated to 1,200°C for 3 h in electrical furnace. The melt samples were pour in graphite plates and afterward annealed at 500°C for 3 h. The glass samples were cut in the size about $1.0 \times 10 \times 0.3$ cm^3 and were rubbed for suitable to analysis. The density (ρ) of glasses were measured by using Archimedes's principle and using these relation, $V = M/\rho$ for calculated the molar volume (V) of glass samples. The optical spectra were measured by Shimadzu UV-3600 Spectrophotometer in the wavelength of 190-1,100 nm. The optical band gap and Urbach energy were calculated from the observed absorption spectra. The refractive indices (n), is measured by an Abbe refractometer which used light of 589 nm and 1-Bromonaphthalin as contact liquid.

Results and Discussion

The 20CaO-(80-x)B_2O_3-xZnO glasses are shown high transparency and colourless as shown in the Figure 1. The glass samples are shown high transparency and colourless.

0.0 mol% x = 5.0 x = 15.0 x = 20.0

Figure 1. 20CaO-(80-x)B_2O_3-xZnO glass samples.

The densities and molar volumes of the 20CaO-(80-x)B_2O_3-xZnO glasses are shown in Table 1. The density of glasses tends to decrease with increasing of ZnO concentration. It means glass losing the compactness in network. The molar volume of glasses tend to increase with increasing of ZnO doped concentration. This can be explained that Zn^{2+} ion destroy the bridges that connect oxygen ions and generate more non-bridging oxygen (NBOs) in glass network. These NBOs produce interstitial space and the molar volume expansion in glass.

Table 1. The densities and molar volumes of the 20CaO-(80-x)B_2O_3-xZnO glasses.

ZnO concentration (mol%)	Density (g/cm^3)	Molar volume (cm^3/mol)
0	3.0229	22.1340
5	2.8893	23.3612
15	2.6510	25.9051
20	2.7586	25.1074

The optical spectra of the 20CaO-(80-x) B_2O_3-xZnO glass samples are shown in Figure 2. The optical absorption edges are not sharply according to their amorphous nature[12]. In amorphous materials, the relation between the absorption coefficient (α(ν)) and photon energy ($h\nu$); $\alpha h\nu = B(h\nu - E_g)^r$, where r is constant and E_g is the optical band gap energy. The r value can be 2, 3, 1/2 and 1/3 for indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively [13-15].

In this glass systems, the above equation depicts a straight line for indirect allowed (n=2) and direct allowed transition (n=1/2). The calculated value for both indirect and direct band gap of glasses are presented in Table 2 and Figure 3.

Table 2. Indirect band gap, direct band gap and Urbach energy of the 20CaO-(80-x)B_2O_3-xZnO glasses.

ZnO concentration (mol%)	Indirect band gap (eV)	Direct band gap (eV)	Urbach energy, ΔE (eV)
0	3.5507	3.8101	0.2500
5	3.5761	3.8201	0.2562
15	3.5920	3.8349	0.2589
20	3.6213	3.8885	0.2594

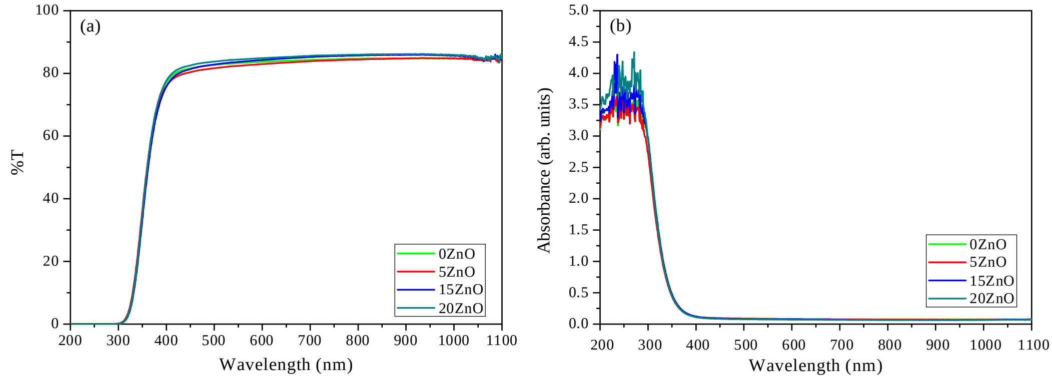

Figure 2. Optical spectra of the 20CaO-(80-x)B_2O_3-xZnO glasses (a) transmission spectra (b) absorption spectra.

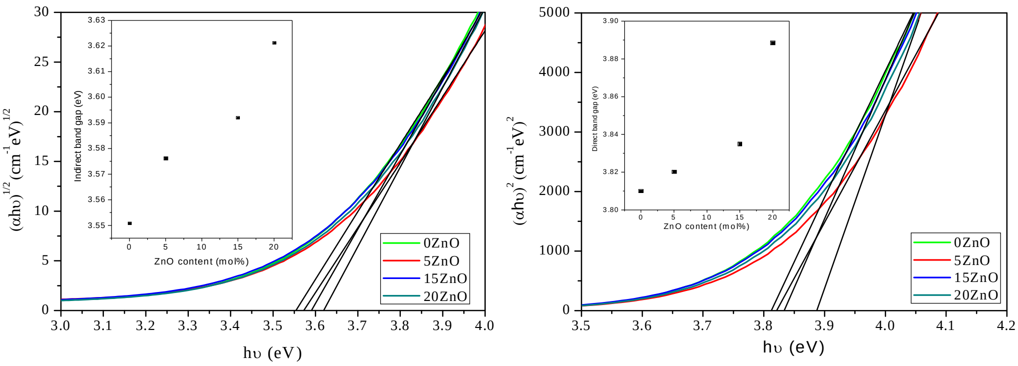

Figure 3. Variation of $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ with hν for the 20CaO-(80-x)B_2O_3-xZnO glasses. Inset shows variation of Urbach energy values with ZnO concentrations for glasses.

The indirect and direct band gaps are found to be in the range of 3.5507 to 3.6213 eV and 3.8101 to 3.8885 eV, respectively. It can be seen from inset figures the both indirect and direct band gap are expanded as the ZnO concentration increase. The increment of both value might be influenced by the bonding defect as well as the existence of NBO in the glass systems. This result is similar with published literature by S.Selvi[15] and M.N. Ami[16] in case of Dy^{3+} doped in borotellurite and boro-teluro-phosphate glasses. Urbach reports that absorption coefficient may depends exponentially on the photon energy of materials. The Urbach energy is given by; α(ν) = B exp ($h\nu/\Delta E$) where B is constant and ΔE is the Urbach energy related to the optical transition between the localized tailed states adjacent to the valence band and conduction band which extends into the band gap[14-16]. From the curves of ln(α), against photon energy $h\nu$ for the 20CaO-(80-x)B_2O_3-xZnO glasses are shown in Table 2 and Figure 4. The Urbach's energy is calculated taking the reciprocals of the slopes of the linear portion of these curves. ΔE values are found to be increased between 0.2500 to 0.2594 eV with the increasing of Zn^{2+} ion content in the present glasses as can be seen in the inset Figure 4. It is due to the rising of disorder /defects degree in glass network via Zn^{2+} ion addition [17].

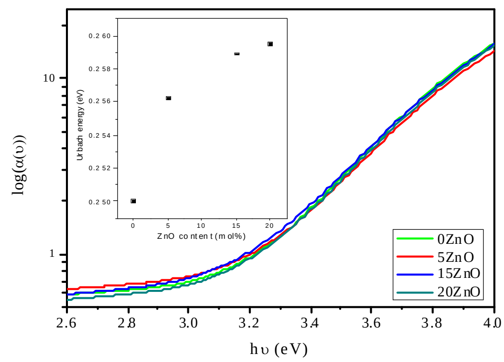

Figure 4. hν versus Ln(α) plot of the 20CaO-(80-x) B_2O_3-xZnO glasses.

The polarizability of the oxide ion was calculated using equation $\alpha_0^{2-} = \left[\frac{R_m}{2.52} - \sum \alpha_{cat}\right] / N_0^{2-}$ where R_m is molar refraction, $\sum \alpha_{cat}$ denotes the molar cation polarizability and N_0^{2-} denotes the number of oxide ions in the chemical formula. In multi-component oxide glasses, the optical basicity was calculated based on the equation proposed by Duffy and Ingram [(9-11)]. as given by $\Lambda_{th}=x_1\Lambda_1 + x_2\Lambda_2 + \ldots$, where Λ_1, Λ_2 are basicities of the oxide components, and x_1 , x_2 are their equivalent fractions. The refractive index, polarizability and optical basicity of the 20CaO-(80-x)B_2O_3-xZnO glass samples given in Table 3. The results from the Table 3, The value of refractive index is in the range of 1.577 to 1.620 and are found to be decreased when filled the ZnO in these glass compositions. It corresponds to the reduction of glass density that light can be move faster in glass network. The polarizability and optical basicity of glass samples are increased when increasing the concentration of ZnO in the range of 1.149 to 1.46 (Å^3) and 0.217 to 0.527, respectively. The increasing of the polarizability is expected as the result of the rise of non-bridging oxygen in the glass matrix. The increase of polarizability results in the increase of optical basicity is good agreement with Duffy[(9-11)] (Figure 5). The optical basicity increment means the higher ability of oxide ions to transfer electrons to the surrounding cations [(14)].

Table 3. Refractive index, polarizability and optical basicity of the 20CaO-(80-x)B_2O_3-xZnO glasses.

ZnO concentration (mol%)	Refractive index	Polarizability (Å^3)	Optical basicity
0	1.6200	1.1494	0.2171
5	1.6042	1.2313	0.3137
15	1.5772	1.4212	0.4949
20	1.5911	1.4611	0.5270

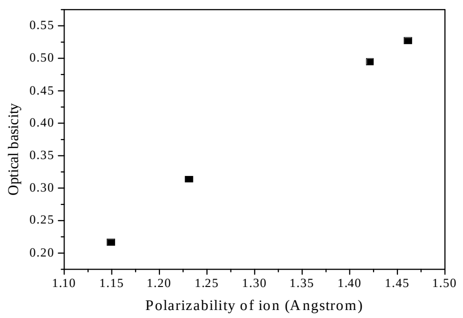

Figure 5. Optical basicity as a function of polarizability of the oxide ion.

Conclusions

The physical and optical properties of the 20CaO-(80-x)B_2O_3-xZnO glass samples (where x=0, 5, 15 and 20 mol%) have been investigated. The density reduction result to decrease in refractive index. The molar volume, optical band gap and polarizability increment with addition of ZnO concentrations represent the modifier behaviour of Zn ion that creates NBOs in glass network. This corresponds with Urbach energy enlargement showing higher level of defect/ disorder existence in network.

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