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Comprehensive study on compositional dependence of optical band gap in zinc soda lime silica glass system for optoelectronic applications

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ABSTRACT

Zinc soda lime silica (ZnO-SLS) glass system with composition x(ZnO)100-x(SLS) (x = 0, 10, 20, 30, 40 and 50 wt.%) were synthesized by the conventional melt-quenching technique. The structural and optical properties of the glasses are measured using X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM) and UV–Visible (UV–Vis) absorption spectroscopy. The optical band gaps were determined by analyzing the optical absorption edge using the Mott-Davis model. A differential method based on Mott-Davis model are used to obtain the type of transition and optical band gap (E_{opt}) which in turn was compared with the value of E_{opt} obtained using the extinction coefficient. The analysis shows that in ZnO-SLS glasses, the optical band gap arises due to direct forbidden transition. Progression of ZnO content cause the absorption edge shifts toward longer wavelengths and decreases the optical band gap. This behavior can be explained in terms of changes to the Zn—O chemical bonds with glass composition. Furthermore, in the case of glasses containing increasing amounts of ZnO, a change of the role of zinc ions in the glass matrix was confirmed from the modifier to a structure-forming component.

1. Introduction

Soda lime silica (SLS) glasses are an interesting material especially in connection with their various applications and the most prevalent type of glasses and commonly used for window glass panes and glass containers but also containment of radioactive waste, as degradable tissue and bone scaffolds within the human body and also development in vitreous glass-ceramic applications [1–5]. Such a wide-ranging of SLS glass applications results from the innovation and possibility of wide range modifications of their chemical composition.

Recently, glass containing zinc oxide (ZnO) is one of the most ideal glass constituents due to their decent physical and mechanical properties with low softening point compared to others glass system [6–8]. This type of glass when doped with transition metal or rare earth ions have a properties such as high transparency from UV to IR region, low refractive index and thermal expansion coefficient with high thermal stability and possibility of incorporating large number of dopant ions are suitable for many potential applications such as favorable material for optical host in solid-state laser [9]. The influence of ZnO on the structure of glasses is unique since they can act as network formers as well as network modifiers [10–13]. The different of ZnO concentrations can strongly influence the structural and optical properties of the glasses. Hence, studying the optical properties, in particular, the optical absorption and energy band gap of ZnO-SLS glasses and how these properties vary with glass composition bring great interest for practical applications. A spirited discussion occurred in the literature and works according to the influence of ZnO content in the borate, tellurite and phosphate glass system [14–16]; however the effect of increasing ZnO concentration into the SLS glass system was inadequate with no briefly explanations to the fundamental topics. Although many properties of SLS glass such as high insulating properties, good and acceptable mechanical have attracted a number of researchers because of their wide-ranging industrial and technical applications, less systematic study on structural and optical properties of SLS glass with addition of ZnO has been reported.

In the present work, the investigation on the effect of compositional dependence on structural and optical properties of ZnO-SLS glass for a

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broad range of glass compositions. The influence of ZnO content on the density, structural, absorbance and optical band gaps are analyzed and discussed.

2. Experimental

A series of zinc soda lime silica glass with the composition x(ZnO)100-x(SLS) with x = 0, 10, 20, 30, 40 and 50 wt.% have been prepared using conventional melt quenching technique. The x values was varied in steps of 10 wt.% producing six glass samples for ZnO-SLS glass system, respectively. Usually, glass may have different value and wide range of melting points depending on their oxide composition. In this study, the mixture is melted at selected temperature that is 1400 °C for 2 h. As all the substances melted, the substances were poured immediately into a container that contained water to obtain a transparency glass frits and then the glass frits were ground in a vibratory mill jar to obtain fine glass powder (<45 μm).

The density of the glass sample was measured by the Archimedes technique using acetone as an immersion liquid. The amorphous nature (glass phase) of the glass samples was confirmed by XRD characterization using Philips X-ray diffractometer (Philips, PW3040/60) with Cu-Kα radiation in the 2θ range from 10° to 90° using 0.02° steps. In this work, a high-resolution FESEM (FEI NOVA NanoSEM 230) was used to observe the microstructure of freshly fractured surfaces of the glass samples.

The optical absorption spectra of the glass samples were recorded at room temperature using UV–Vis spectrophotometer (Lambda 35, Perkin Elmer) in the wavelength region from 300 to 800 and these measurements are made on glass and glass ceramic powder with size ≤63 μ that have been compressed in a specific holder. However, there was a limitation when using this technique which is the particle size need to be small and fine about <20 μm so that the precise data can be achieved. The application of the Tauc plot method has been used widely to determine band gap energy by using the diffuse reflectance spectrum as shown;

$$(\alpha h\nu)^{1/n} = B(h\nu - E_{opt}) \quad (1)$$

where α is absorption coefficient, h is Planck's constant, ν is frequency of vibration, B is proportional constant and E_{opt} is the optical band gap. From the specific software inside the UV–Vis computer, the obtained diffuse reflectance spectrum was converted to Kubelka-Munk function. Thus, the vertical axis was converted to quantity F(R∞), which is proportional to the absorption coefficient. The α in the Tauc equation was substituted with F(R∞) hence the relational expression becomes:

$$(F(R\infty)h\nu)^{1/n} = B(h\nu - E_{opt}) \quad (2)$$

In order to find the type of transition, the E_{opt} values are calculated by extrapolation of the linear parts of $(\alpha h\nu)^{1/n}$ vs. $h\nu$ curves to $(\alpha h\nu)^{1/n} = 0$ for different values of transition. Here, the unit of $h\nu$ is eV (electron volts), and its relationship to the wavelength λ (nm) becomes $h\nu = 1239.7/\lambda$. Later, a line is drawn tangent to the point of inflection on the curve, and the $h\nu$ value at the point of intersection of the tangent line and the horizontal axis is determined the E_{opt} values. The type of transition can be obtained from the value of n.

3. Results and discussion

A series of ZnO-SLS glass frits were successfully melted and formed into a glass from pure ZnO powder and SLS glass waste powder via conventional melt and quenching technique. Most of the glass frits were transparent, light greenish in color, bubble-free and homogeneous. The color of the glass frits become more greenish with increasing of ZnO content.

Table 1
Chemical composition of ZnO-SLS glass system (wt.%).

Glass sample/oxide	SLS	10ZnO 90SLS	20ZnO 80SLS	30ZnO 70SLS	40ZnO 60SLS	50ZnO 50SLS
SiO_2	69.5	62.6	55.6	48.7	41.7	34.9
Na_2O	12.5	11.3	10.0	8.8	7.5	6.3
CaO	11.3	10.2	9.1	7.9	6.8	5.7
Al_2O_3	2.8	2.4	2.2	1.9	1.6	1.3
MgO	2.0	1.9	1.7	1.5	1.3	1.0
K_2O	1.5	1.3	1.2	1.1	0.9	0.7
ZnO	–	10.0	19.9	29.8	39.9	49.8
Others	0.4	0.3	0.3	0.3	0.3	0.3
Total	100	100	100	100	100	100

The chemical composition of precursor glasses were analyzed by Energy Dispersive X-ray Fluorescence (EDXRF). The chemical analysis can be seen in Table 1 and all the elements are measured in oxide form. As can be seen in Table 1, the major components of the precursor glass are ZnO, SiO_2, CaO and Na_2O which these oxide elements comprise around 95 wt.% from the total weight composition of the precursor glasses. Other oxide elements such as K_2O and MgO are minor constituents and account for a small percentage of the bulk composition. All other elements such as BaO, Cr_2O_3, Fe_2O_3, and B_2O_3 collectively seldom exceed 1 wt.% of the bulk composition. The addition of ZnO content into the SLS glass matrix has affected the percentage of other elements. The increase of ZnO content in the precursor glasses has decreased the percentage of other major oxides such as SiO_2, CaO and Na_2O. The decrease of these oxides has been optimized principally for physically and elasticity and has a good durability provided by the low CaO content. The EDXRF analysis shows that with the progression of ZnO content into the SLS glass has decrease the percentage of other major elements in the precursor glass samples. The composition of SiO_2 element is decrease from 69.5 to 34.9 wt.%, Na_2O decrease from 12.5 to 6.3 wt.% and CaO decrease from 11.3 to 5.7 wt.%. Other elements in the glass samples also decrease with the addition of ZnO content. As shown in the Table 1, the percentage of Al_2O_3 decrease from 2.8 to 1.3 wt.%, K_2O decrease from 1.5 to 0.7 wt.% and MgO decrease from 2.0 to 1.0 wt.%.

Density is a tool in revealing the degree of change in the structure with the change in the glass composition. The average density was frequently measured in order to understand the molecular packing inside the material. The density of the glass samples was measured using the Archimedes technique. A plot of density of ZnO-SLS glass sample is shown in Fig. 1. As shown in Fig. 1, the density of the glasses is increases from 2.520 to 2.842 g/cm^3 with the addition of ZnO content. The increasing in density of the glasses is due to the heavier Zn atomic mass compare to the other element in the glass samples [16]. The atomic mass of Zn is 65.390 amu which is heavier compare to the atomic mass of Si (28.086 amu), Ca (40.078 amu) and Na (22.989 amu). Besides, an increase of density of the glass samples also results in the changes of the crosslink density [17]. The increases in density of the

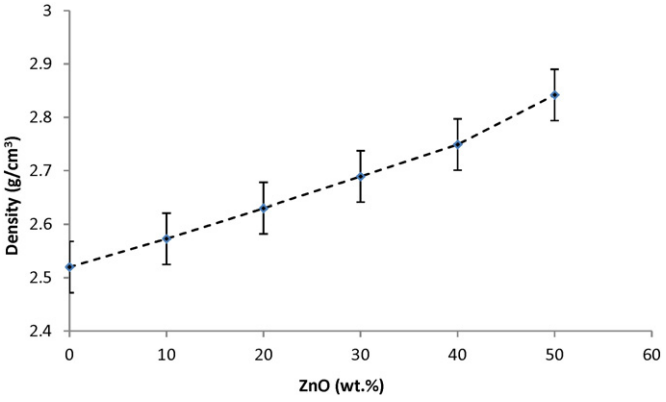

Fig. 1. The average density of ZnO-SLS glass system.